30 April, 1976

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FINAL SCIENTIFIC REPORT

ENERGY MIGRATION INVOLVING IRRADIATED SOLIDS

Period Covered

1.IV. 1971 to 31.III. 1976

Professor Joseph Cunningham,
University College Cork,
Ireland.

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TECHNICAL SUMMARY

(Dates relate to attached Chronological list)

One particular aspect of 'Energy Migration in Irradiated Solids' has been emphasised in this research, namely the migration of energy from an irradiated solid to acceptor molecules of another phase in contact with the surface of the irradiated solid. Convincing evidence for this type of energy migration has been developed from studies at both "GAS/IRRADIATED SOLID" and "LIQUID/IRRADIATED SOLID" interfaces.

Initially (1972 and 1973) studies of such interfaces were made with closed systems under continuous illumination at low intensity. Using UV-photons of wavelengths absorbed by the solid substrate but not by the acceptor molecules in contact with the surface, kinetics and mechanisms of photoassisted chemical changes were established for the systems: Aqueous Electrolytes/ZnO ; gaseous Methyl Halides/ZnO . An inherent limitation of the studies on closed systems with continuous low intensity illumination was their inability to distinguish between *fast* and slow photoassisted processes. Conclusions therefore rested upon detailed chemical study of long-term changes in acceptor molecules, brought about slowly by uv-illumination.

Later the technique of electron spin resonance was successfully applied, for the first time, to continuously circulating aqueous suspensions of zinc oxide in order to provide new insight into *fast* changes occurred simultaneously within the illuminated semi-conducting solid. (1973, '74). An important unifying feature of the detailed mechanisms developed for the energy transfer process at these illuminated interfaces was the central role played by charge-transfer processes involving photogenerated electrons and electronic holes. Indications were obtained from these studies that quantum efficiencies of the observed chemical changes depended upon the extent to which electron-hole recombination processes competed with the chemical processes under study.

The research effort entered a new phase in 1975 with the development at U.C.C. of unique apparatus for applying Dynamic Mass Spectrometry and related fast detection techniques to time-resolve processes initiated at GAS/METAL OXIDE interfaces by 50μs pulses of uv-photons. Initial studies of photoassisted interactions of flash illuminated ZnO or TiO_2 with $^{16}O_2$, N_2O or C_2H_5OH were expanded to include studies with isotopically enriched gases $^{18}O_2$, $^{14}N^{15}N^{16}O$ and C_2D_5OD. The technique successfully time-resolved *fast* flash-initiated surface processes (such as surface photolysis, or photodesorption of chemisorbed oxygen, or release of alkene products from alcohol photodehydration) from *slower* surface processes, (such as post-flash uptake of oxygen by active surface sites, or release of products of alcohol photodehydrogenation). These studies have resulted in extended publications (1975 and 1976)* describing in detail this interesting new technique and the type of results which can be obtained from it. Implications of these results for 'Energy Migration within Solids and across their Interfaces' will be presented at a Conference to be held under that title at University College Cork in September 1976.

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* Copies of the four most recent scientific papers in 1976 are appended to this report since, unlike other publications listed on the following pages, copies have not previously been supplied to EOAR and AFOSR.

Chronological Bibliography of Papers and Communications arising from Research carried out, in part, with financial support under Grant AF-2148.

1976 - PUBLICATIONS

**Flash initiated Surface Reactions on ZnO and TiO_2 studied by Dynamic Mass Spectrometry*

Joseph Cunningham and Nicolas Samman

Chapter 17 in Volume 4 *Dynamic Mass Spectrometry* (Editors, Price and Todd) Pages 247-271. Published 1976 Heyden and Sons. London.

**Photoeffects involving Oxygen-18 at flash-illuminated ZnO and TiO_2 Surfaces*

Joseph Cunningham, B. Doyle and N. Samman

JCS Farad. Trans. I (1976) Vol. 72 1495-1498.

1976 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS

**Oxygen Intermediates at flash-illuminated Metal Oxide Surfaces studied by Dynamic Mass Spectrometry*

Joseph Cunningham, B. Doyle, D.J. Morrissey and N. Samman

Paper accepted for presentation at *Sixth International Congress on Catalysis*, London, July 1976.

**Active Sites for Dehydration and Dehydrogenation of Aliphatic Alcohols over ZnO and TiO_2 at 15-30^{o}C*

Joseph Cunningham, K. Hodnett, Paul Meriaudeau and D.J. Morrissey

Paper accepted for presentation at *Fifth Iberoamerican Symposium on Catalysis*, Lisbon, July 1976.

Processes contributing to Energy Dissipation at Surfaces of Flash-illuminated Metal Oxides

Joseph Cunningham

To be presented at EUCHEM Conference on "Migration of Charge and Energy within Solids and at their Surfaces" 22-24 September, Cork, Ireland.

1975 - PUBLICATIONS

Photoassisted Surface Reactions Studied by Dynamic Mass Spectrometry
Joseph Cunningham, Eoin Finn and Nicolas Samman
Faraday Discussions of the Chemical Society No. 58, pages 160-174.

Reactions Involving Electron Transfer at Semiconducting Surfaces: VI. Electron Spin Resonance Studies on Dark and Illuminated Aqueous Suspensions of Zinc Oxides
Joseph Cunningham and Sean Corkery
Journal of Physical Chemistry, (1975), 79, 933-941.

1975 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS

Fast-detection Studies of Radiation-induced Effects at Aqueous Electrolyte/Metal Oxide Interfaces
Presented by Joseph Cunningham to an informal Symposium at Max Planck Institute fur Biophysikalische Chemie, Berlin, February, 1975.

Dynamic Mass Spectrometry applied to Flash-initiated events on ZnO
Presented by Joseph Cunningham at an informal Symposium on ZnO at Free University Berlin, February 1975.

1974 - PAPERS PUBLISHED

Reactions Involving Electron Transfer at Semiconductor Surfaces: V. Reactivity and Electron Paramangnetic Resonance of Electron Transfer sites on Rutile
Joseph Cunningham and Anthony L. Penny
Journal of Physical Chemistry, (1974), 78, 870-875.

New Technique for the Study of Selective Reactions at Rutile Surfaces
Joseph Cunningham, Eoin Finn and Anthony L. Penny
Chemica Scripta, (1974), 6, 87-88.

1974 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS

Flash-initiated Surface Reactions studied by Dynamic Mass Spectrometry
Paper presented by Joseph Cunningham to *Fourth International Symposium on Dynamic Mass Spectrometry* held at University of Salford, July 1974.

1974 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS (Contd)

Photooxidation, Photodehydrogenation and Photodehydration on Metal Oxide Catalysis
delivered by Joseph Cunningham to Conference on *Modern Developments in Industrial Catalysis* at Imperial College London, July 1974.

Photoassisted Surface Reactions studied by Dynamic Mass Spectrometry
presented by Joseph Cunningham to Faraday Discussion on *Photoeffects in Adsorbed Species* held at Cambridge, England, September 1974.

1973 - PUBLICATIONS

ESR Studies of Aqueous Suspensions of Zinc Oxide
Joseph Cunningham and Sean Corkery
Chemical Phys. Lett., (1973), 21, 421-425.

1973 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS

Role of Surface Charge in Reactions at METAL OXIDE/AQUEOUS ELECTROLYTE Interfaces
Presented by Joseph Cunningham as Paper No. 7 at a Faraday Society Informal Discussion at University College Cork, 4 & 5 January, 1973.

Roles of Surface States and Surface Charge in Reactions at METAL OXIDE/GAS Interfaces
Presented by A.L. Penny as Paper No. 16 at a Faraday Society Informal Discussion held at University College Cork, 4 & 5 January, 1973.

Processes at Semiconductor Surfaces studied by Fast Detection Techniques
Presented by Joseph Cunningham at Informal Seminar in Universite Claude Bernard, Villeurbanne, Lyon. September 1973.

1972 - PUBLICATIONS

Reactions Involving Electron Transfer at Semiconductor Surfaces: IV. Zinc Oxide promoted Photoreductions in Aqueous Solutions at Neutral pH
Joseph Cunningham and Hanaa. Zainal
Journal of Physical Chemistry (1972), 76, 2362-2374.

Reactions Involving Electron Transfer at Semiconductor Surfaces: III. Dissociation of Methyl Iodide over Zinc Oxide
Joseph Cunningham and A.L. Penny
Journal of Physical Chemistry (1972), 76, 2353-2361.

1972 - PAPERS COMMUNICATED TO SCIENTIFIC MEETINGS

Energy Transfer at Semiconductor Surfaces
Presented by Joseph Cunningham at Philips Research Laboratories, Eindhoven, 6 April, 1972.

Energy Migration in Irradiated Solids
Presented by Joseph Cunningham at AFOSR Contractors Meeting, Santa Birbara, California, September 1972.

Chapter 17

Flash-Initiated Surface Reactions on Zinc Oxide and Titanium Dioxide Studied by Dynamic Mass Spectrometry

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1. Introduction

This chapter describes results of experiments in which fast-response mass spectrometric detection is applied to the study of photoeffects at the surfaces of metal oxide catalysts. No major development or innovation in dynamic mass spectrometer technique was needed for the experiments described. Emphasis has been concentrated, rather, on exploring the advantages and limitations inherent in application of routine dynamic mass spectrometric techniques to the study of transient changes in gas composition produced by pulses of UV illumination incident on catalyst surfaces. Zinc oxide and titanium dioxide were selected for study as representative semiconducting metal-oxide catalysts, because of the availability of extensive background information on their surface and catalytic properties and how these are affected by UV illumination.[1-9] This literature indicates that changes in composition of the gas phase above UV-illuminated metal-oxide catalysts may originate from: (i) photolysis of surface layers;[1] (ii) photoassisted decreases or increases in the number of adsorbed molecules or ions on the illuminated surface (termed photodesorption and photoadsorption, respectively, photosorption collectively);[5] (iii) enhanced reaction between the illuminated surface and components of the gas phase (termed photo-assisted gas/surface reaction); (iv) enhanced catalytic activity of the illuminated surface in promoting reaction between components adsorbed onto the metal

Table 1. Processes reported to affect gas phase above UV-illuminated zinc oxide or titanium dioxide.

Process	Reference
PHOTOLYSIS OF SURFACE LAYER	
$ZnO + h\nu \longrightarrow ZnO^* \longrightarrow Zn^* (s) + 1/2O_2 (g)$	1
PHOTOSORPTION	
$xO_2 (ads)/TiO_2 \overset{h\nu}{\rightleftharpoons} O_2 (g) + (x-1) O_2 (ads)/TiO_2$	5,10
PHOTOASSISTED GAS-SOLID REACTION	
$ZnO^* + N_2O (ads) \longrightarrow N_2 (g) + O^- (ads)/ZnO$	58
$HO^-/ZnO^* + CD_3I (g) \longrightarrow I^-/ZnO + CD_3H$	59
PHOTOCATALYSIS	
$1/2O_2 (g) + CO (g) + ZnO^* \longrightarrow CO_2 (g) + ZnO$	4, 5, 6

oxide from the gas phase (termed photocatalysis).[4-6] The examples of these processes given in Table 1 were measured by various workers using continuous low-intensity UV illumination, whereas the new work described in this chapter has been mainly carried out with high-intensity pulses of UV illumination with duration ca. 50 μs. A brief review of published work on photoeffects at gas/metal oxide interfaces relevant here, both as an introduction to the nature of gas—metal oxide interactions and in identifying mechanisms by which UV photons modify such interactions. Since photoeffects involving oxygen have received particularly extensive attention in the literature, it will be convenient to treat these separately in Section 2 of the present chapter and then to present data on other gases in Section 3.

2. Photoeffects involving oxygen at zinc oxide and titanium dioxide surfaces

A. INTRODUCTION

An oxygen deficiency has been reported for zinc oxide and titanium dioxide surfaces[3,6,7] and particularly for samples preactivated in vacuum at 400°C such as were investigated in the present study. Experimental observations on photoeffects over titanium dioxide surfaces exposed to continuous UV illumination have been variously interpreted as providing support for each of the processes listed in Table 1. Several workers have demonstrated by ESR and partial pressure analysis that surface photolysis occurred with formation of surface Ti^{3+} centres.[3,4,8] Photodesorption of preadsorbed oxygen has also been reported[4,9] over reduced surfaces. The reverse process of oxygen photoadsorption has been observed[9,10] and correlated with the surface concentration of Ti^{3+} species on reduced titanium dioxide samples or with surface hydroxyls on fully oxygenated surfaces.[10] The UV-illuminated titanium dioxide surfaces also catalyse partial oxidation of hydrocarbons.[11]

For zinc oxide surfaces the following parameters have been reported as determining whether photoadsorption or photodesorption predominate: oxygen partial pressure;[12] extent of metal excess non-stoichiometry;[5] concentration of conduction band electrons; and position of the Fermi level.[13,14] Correlations between photodesorption and photoconductivity are required by various models for migration and trapping of electronic holes at the illuminated interface,[15-17] and Melnick has reported such correlations.[18] Since photoconductivity studies have revealed 'fast' and 'slow' photoprocesses, photosorption processes may likewise be expected to exhibit fast and slow components. It has recently been suggested by Tanaka and Blyholder that the slow step in photocatalytic oxidation of carbon monoxide over zinc oxide is formation of O^- ions on the surface.[19] Photolysis of zinc oxide has also been reported and evidence presented that presence of excess metal or of electron-trapping species may modify surface photolysis,[20] as has been reported for NaN_3.[21]

Finally, a brief summary of current ideas on how surfaces of zinc oxide and titanium dioxide samples may be modified by adsorbed oxygen is appropriate in this introduction. Electronic theories of chemisorption describe such modifications in terms of 'collective electron' energy levels at and close to the surface.[5,22,23] Figure 1(a) illustrates the energy-band model applicable within the bulk lattice of non-stoichiometric zinc oxide or titanium dioxide. Outgassing these materials *in vacuo* to temperatures of 300—400°C, as was used to precondition surfaces in the present study, is reported to enhance extent of metal-excess non-stoichiometry in surface layers, above that in the bulk.[3,7] Such additional surface excess of ionizable donors is schematically denoted in Fig. 1(b) and can result in excess positive charge close to the surface, with a corresponding enhancement of electrons in the conduction band within the bulk. According to the 'collective electron' description, such separation of charge should result in downward bending of energy bands as illustrated in Fig. 1(b). A situation formally similar to that in Fig. 1(b) can result if adsorbed atoms, molecules or ions inject electrons into the bulk conduction band in the process of adsorption, thereby leaving positively charged species at the surface. Hydrogen, carbon, monoxide and some oxygenated hydrocarbons are reported as adsorbing onto zinc oxide with release of electrons,[24,25] which corresponds to cumulative chemisorption and tends to produce downward band-bending as in Fig. 1(b).

Oxygen adsorption onto zinc oxide or titanium dioxide is reported as giving rise to

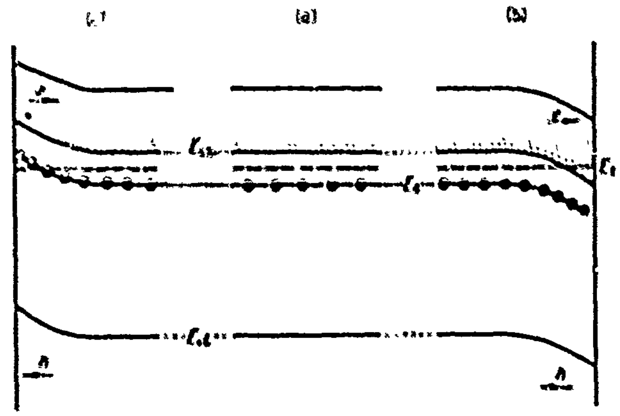

Fig. 1. 'Collective electron' description of electron energy levels within the bulk or in the surface regions of non-stoichiometric *n*-type ZnO and TiO_2. $E_{c.b.}$ and $E_{v.b.}$ denote, respectively, the lowest energy level in the conduction band or highest in the valence band, and $E_{c.b.} - E_{v.b.} \sim 3$ eV. E_d denotes energy levels of donor centres such as excess metal and E_f represents the equilibrium Fermi level. (a) Situation within the bulk or near the surface in 'flat-band' conditions. (b) Surface positive with respect to bulk, with downward band bending such as may arise from cumulative chemisorption. (c) Surface negative with respect to bulk, with upward band bending such as may originate from depletive chemisorption.

depletive chemisorption, which envisages each chemisorbed oxygen as localizing an electron from the conduction band as the sites of adsorption.[24] The resultant excess negative charge at the surface, due to species resembling O_2^-, O^- or O^{2-}, may be represented in collective electron descriptions as producing the upward bending of energy bands near the surface depicted in Fig. 1(c). Direct evidence in support of this representation has come from measurements showing increasingly negative surface potential on cadmium sulphide (CdS) single crystals in the dark at increasing oxygen pressures,[28] and from direct ESR evidence for the formation of O_2^- on zinc oxide[11,16] and titanium dioxide.[3] Indirect evidence for depletive chemisorption of oxygen onto zinc oxide samples as O_2^- or O^- ions has been deduced from oxygen-induced decreases in electrical conductivity of zinc oxide samples,[29-31] using the criterion that increased resistivity of the samples reflects fewer mobile electrons. On the basis of this criterion, measurements of changes in electrical conductivity accompanying adsorption have been widely used as a convenient indicator to the depletive or cumulative nature of gas-semiconductor interactions. Serious questions as to the validity of this criterion, at least for titanium dioxide samples, have been raised by Crucq and Degols on the basis of their studies on the frequency dependence of conductivity on rutile.[32]

Direct observations have been reported on the influence of oxygen on surface potential of zinc oxide during oxygen photosorption.[33] Decreases in the number of surface O_2^- radicals have been directly monitored by ESR during oxygen photodesorption from zinc oxide.[16,34] In terms of collective electron models of the O_2/metal oxide interface, such oxygen photodesorption effects have been related to the following processes:

Depletive chemisorption in the dark:

$$O_2(g) \rightleftharpoons O_2(ads) \overset{e^-_{c.b.}}{\rightleftharpoons} O_2^-(ads) \quad (1)$$

Photoactivation of the metal oxide (MO):

$$MO + h\nu \rightarrow (e + h)/MO^* \rightleftharpoons e^- + h^+ \quad (2)$$

Interaction of adsorbed oxygen with photogenerated species:

$$O_2^-(ads) + h^+ \rightarrow O_2(g)/MO^* \rightarrow O_2(g) + MO \quad (3)$$

or

$$O_2^-(ads) + (e + h)/ZnO^* \rightarrow O_2(g) + h^+/ZnO \quad (4)$$

Process (1) should give rise to the upward band-bending depicted in Fig. 1(c). This band-bending should in turn attract holes photogenerated by (2) towards the surface, there to react with oxygen ions via (3) or (4) and thereby decrease the negative surface potential below that established by (1) in the dark.

Direct ESR evidence for photoinduced increases in numbers of O_2^- radicals on titanium dioxide has been obtained during photoadsorption of oxygen.[31] These and other oxygen photoadsorption effects have been analysed for agreement with collective electron models,[11-17] but the rather complex treatments needed to account for observed results[9] are beyond the scope of this brief introduction. It must, however, be noted that increasing emphasis has been given in recent years to alternative models of real surfaces which emphasize special properties of unique localized surface sites[33,34] rather than collective-electron properties of the entire surface. On zinc oxide or titanium dioxide localized surface sites with characteristically high activity for chemisorption, catalysis or photoeffects may take several forms: *surface defects* (such as oxygen vacancies on titanium dioxide or excess metal on both zinc oxide and titanium dioxide); *surface impurities* (such as altervalent ions or adsorbed oxygen ions on zinc oxide and titanium dioxide); or *surface states* (originating because the surface is necessarily a discontinuity and components of an otherwise ideal lattice situated at such a discontinuity must posses partially unsaturated valencies and/or incompletely compensated charges).[34] Evidence for the occurrence and migration of oxygen vacancies in titanium dioxide samples has come from many studies,[3,37,38] but results on zinc oxide do not favour existence of oxygen vacancies in that material, except after exposure to irradiation by high-energy radiations or electrons.[39] ESR evidence has been reviewed[9] for Ti^{3+} radical ions on the surface of titanium dioxide. Recent results of catalytic studies support high activity of metal-excess surface sites on titanium dioxide[40] and zinc oxide.[41,42] Zinc-rich surfaces of zinc oxide have been obtained by cleaving ZnO single crystals in high vacuum and are reported to exhibit markedly different properties from the geminate oxygen-rich surface simultaneously produced by cleavage.[43,44] Recent papers by Gatos and co-workers[45,46] demonstrate the marked influence which a high density of surface states can exert on photoeffects in zinc oxide. They observe, in the presence of species adsorbed onto zinc oxide from air, photoinduced transition of electrons from the zinc oxide valence band into surface states ca. 2 eV below the conduction band. These transitions gave rise to an increase in surface potential. Since this is opposite to the effect expected from collective electron models (e.g. via processes 3 or 4), it has been termed by Gatos and co-workers the 'photovoltage inversion effect'.[45] This and related effects involving surface states and other unique surface sites are likely to be important in the present work in which UV-visible and IR photons are incident on zinc oxide and titanium dioxide surfaces. It should particularly be noted that such effects may be opposite to those expected from the collective electron models.

B. EXPERIMENTAL

The central objective of the present study was to employ mass spectrometric detection to monitor the time profiles of changes in gas composition initiated by the incidence of 50 μs flash of UV light onto zinc oxide or titanium dioxide surfaces. A 15 cm long quadrupole mass analyser tube was used for mass analysis with associated r.f. supply at 4 MHz (for the m/e range 1—50) or 2 MHz (for the m/e range 4—200) and scanning controls (built according to a design of the Department of Electronics and Electrical Engineering, University of Liverpool). A 17-dynode electron multiplier (EM) was found necessary to achieve requisite fast response and sensitivity at unit mass resolution with <5% valley. In order to avoid spurious photoeffects arising from the incidence of stray photons from the illumination system onto the electronmultiplier, a relatively long (1 m) path with several bends was used between the photoreactor and the electronmultiplier. The equipment used is shown diagrammatically in Fig. 2 and resembles the conventional kinetic flash photolysis experiment except that the steady state beam of photons through the reaction vessel via a monochromator to a photomultiplier was replaced in our system by a steady state flow of molecules from the reaction vessel along a bent 1 m flight path to the ion source of the quadrupole mass spectrometer.

With the exception of a 15 cm long, 40 mm OD cylindrical glass window the remainder of the ion-pumped high-vacuum system depicted schematically in Fig. 2 was fabricated from stainless steel. This system routinely attained total residual gas pressures of ca. 10^{-6} N m^{-2} after thermal outgassing. Samples of zinc oxide or titanium dioxide were introduced into this system as thin layers previously deposited onto cylindrical quartz substrates of geometric surface area 0.01 m^2. These metal oxide/quartz samples were located inside the 15 cm long cylindrical 'window', which was of Kodial glass for most experiments and served to prevent light of wavelengths <300 nm from entering the vacuum system. In some experiments a greater proportion of the UV output of the flash-tube was admitted by replacing this Kodial window with a quartz window which transmitted down to 200 nm. When so desired, light of wavelengths <360 nm was effectively excluded from the system, together with much of the IR output, by wrapping a Wratten 38A gelatine filter around the Kodial or quartz windows. It should be noted in Fig. 2 that the electron multiplier and 15 cm quadrupole mass filter were located very close to the ion pump to achieve minimum system pressure at their location. Results described in this paper were all obtained in conditions such that this minimum system pressure did not exceed 10^{-6} N m^{-2}, as indicated by the meter of the ion pump. Reactant gases were introduced to the vacuum system via metal variable-leak valves from an external gas-handling system from which grease and mercury were rigorously excluded. The steady state pressures at various locations in the system was monitored with Bayard-Alpert ionization gauges (cf. Fig. 2) and did not exceed 10^{-3} N m^{-2}. Output of the mass filter at appropriate *m/e* values was linearly related to these pressures over the range 10^{-6}—10^{-3} N m^{-2}. A marked disadvantage of the quadrupole used was that it did not yield 'standard' ion fragmentation patterns, but exhibited a greater sensitivity to low mass numbers. This discrimination necessitated extensive calibration with known gases to obtain reference spectra for comparison, and this was done for all the reactant gases used in the present study.

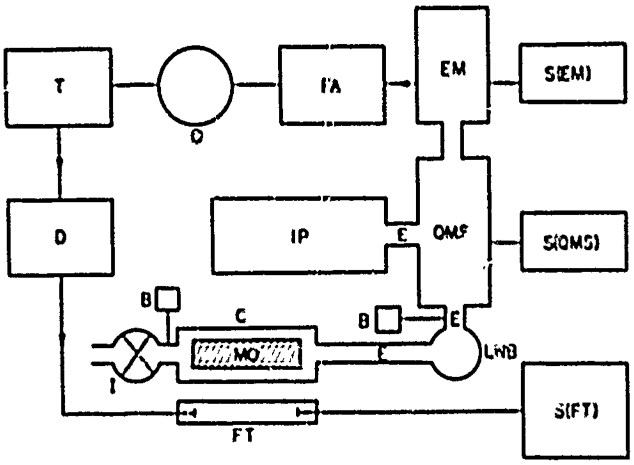

Fig. 2. Dynamic mass spectrometer system for the study of changes in gas phase pressure and composition caused by flash-initiated surface processes. The system consists of: (i) High-vacuum system, comprising: inlet leak valve, I; pressure measuring gauges, B; glass-walled photoreactor, C; metal oxide layer, MO; high-conductance tubing, E; quadrupole mass spectrometer, QMS; 14-stage electron multiplier, EM; ion pump, IP; and liquid nitrogen cooled baffle, LNB. (ii) Fast detection circuitry comprising: trigger unit, T; variable delay line, D; quartz flash-tube, FT; oscilloscope, O; and fast amplifier, FA. (iii) Appropriate electronic supplies: S(EM), S(QMS) and S(FT).

Preparation of materials

The zinc oxide and titanium dioxide materials used in the present study were high-purity powdered samples obtained through the courtesy of the New Jersey Zinc Co. and coded, respectively, as ZnO-SP500-78115 and Rutile-MR-128. Impurity content of these oxides were low (e.g. <0.001% Fe, Cu or Mn in ZnO and <0.07% Cl_2 in TiO_2). Materials were also alike in surface areas (4 and 5.4 $m^2 g^{-1}$), particle sizes (0.2—2 μ) and reflectance spectra (onset of absorbance at ca. 390 nm rising to a maximum at 370 nm). For a few experiments, doped zinc oxide samples were used and corresponded to the ZnO-SP500 material treated to incorporate lithium (termed Li-ZnO) or indium (termed In-ZnO).

Powdered materials were taken into an aqueous slurry with triply distilled water, or occasionally fully deuterated water, and coated onto a quartz substrate as a layer of thickness ca. 10^{-4} m which was dried in a vacuum oven at 110°C before introduction into the vacuum system. After bake-out of the entire apparatus at 250°C until the pressure fell to 10^{-6} N m^{-2}, a small heater was placed around the glass section of the vacuum system to bake out the metal oxide at 250—350°C for 16 h. A sequence of experimental observations on such samples was usually commenced within 1 h of cooling to room temperature. Residual gas analysis indicated $<10^{-6}$ N m^{-2} partial pressure of 'carbon monoxide plus nitrogen' as the major constituents of residual gases in the system but with residual oxygen or water vapour $<10^{-6}$ N m^{-2}.

Reactant gases nitrous oxide, oxygen and hydrogen were spectroscopically pure (BOC Grade X) delivered in Pyrex break-seal vessels which were used as received. Isotopically labelled $^{15}N^{15}N^{18}O$ and C_2D_5OD (either anhydrous or containing 5% D_2O) were supplied by Stohler Isotopes. Oxygen enriched in ^{18}O was obtained from Yida-Miles Laboratories and deuterium (99.9% D_2) from BOC. Anhydrous deuterated methanol and methyl iodide were obtained from Prochem and used as received. Reference mass spectra of each reactant gas, entering the mass spectrometer via a by-pass which did not expose it to the metal oxide, were determined prior to each experiment.

Sample illumination

In order to investigate 'fast' photolysis or photosorption effects, metal oxide/quartz samples were exposed to light pulses of 50 μs duration emitted by an oxygen-quenched xenon flash-tube dissipating 200 J electrical energy per flash. An elliptical reflector housing, enclosing the flash-lamp and the cylindrical glass window of the vacuum system, was used to deliver emitted light to the sample. Substitution of a potassium ferrioxalate actinometer and appropriate filters at the position normally occupied by the metal oxide/quartz samples indicated that 2 × 10^{16} photons in the wavelength range 300—400 nm were delivered to the sample per flash incident through a Kodial glass envelope. With a quartz envelope, the total number of photons with wavelengths 200—500 nm delivered to the sample was 5.4 × 10^{16} per flash.

Fast-detection circuitry

Rapid response in the electron multiplier detector of the mass spectrometer was desired in order to follow any sudden changes in gas composition within the vacuum system, as occasioned by incidence of the high-intensity 50 μs light pulses onto the metal oxide. For this purpose, fast-detection circuitry very similar to that normally employed in flash-photolysis apparatus was utilized (see Fig. 2). The response time of the detector system, with the output of the multiplier fed into an oscilloscope via a low-pass filter (to eliminate 4 MHz or 2 MHz ripple), was 200 μs and was not the slowest step in the response of the system to flash-initiated changes in gas composition. Time-of-diffusion of gas molecules from the flash-illuminated metal oxide interface through the vacuum system to the ion source of the quadrupole appeared to be the rate-limiting step. This follows from data which demonstrated that rise times of ion currents corresponding to various molecular gases generated by light flashes varied in the manner expected for diffusion (i.e. rise time ∝ $m^{1/2}$).

Parallel investigations of photoeffects under long-period, low-intensity UV illumination were carried out, where possible, for comparison with high-intensity flash-initiated processes. For such experiments the outputs of 150 W mercury arc, 250 W mercury—xenon arc or 450 W xenon arc lamps were utilized. For photosorption or photolysis studies, suitably filtered outputs of these lamps were incident on a zinc oxide or titanium dioxide sample suspended from one arm of a high-sensitivity electrobalance. Samples were pre-equilibrated with the adsorbing gas in the dark at pressures ca. 10^{-1} N m^{-2} prior to recording any photoinduced changes in weight. This electrobalance was also utilized to determine the extent of adsorption of the various reactant gases onto zinc oxide or titanium dioxide at room temperature. Adsorption isotherms were thus obtained at higher pressures and extrapolated to conditions of the present experiments in order to estimate the percentage of surface sites occupied by reactant gases prior to UV flashes.

C. RESULTS

Photolysis at 10^{-6} N m^{-2}

In view of literature reports that UV photons incident on zinc oxide and titanium dioxide may cause photolysis to yield molecular oxygen and metal, it was of particular interest to monitor ion currents at the corresponding *m/e* values before, during and after arrival of a high-intensity light pulse onto zinc oxide or titanium dioxide surfaces. The mass filter was, therefore, set to continuously monitor ions with *m/e* 32 and time profiles were measured for changes in ion current caused by arrival of the first pulse delivered to a 'fresh' zinc oxide or titanium dioxide surface under the lowest residual pressure (10^{-6} N m^{-2}) attainable with the vacuum system. The trace shown in Fig. 3(a) was obtained by photographing a slow, appropriately triggered oscilloscope sweep before, during and after flash illumination of a fresh zinc oxide surface through a cylindrical quartz window. It demonstrates a large rise in ion current

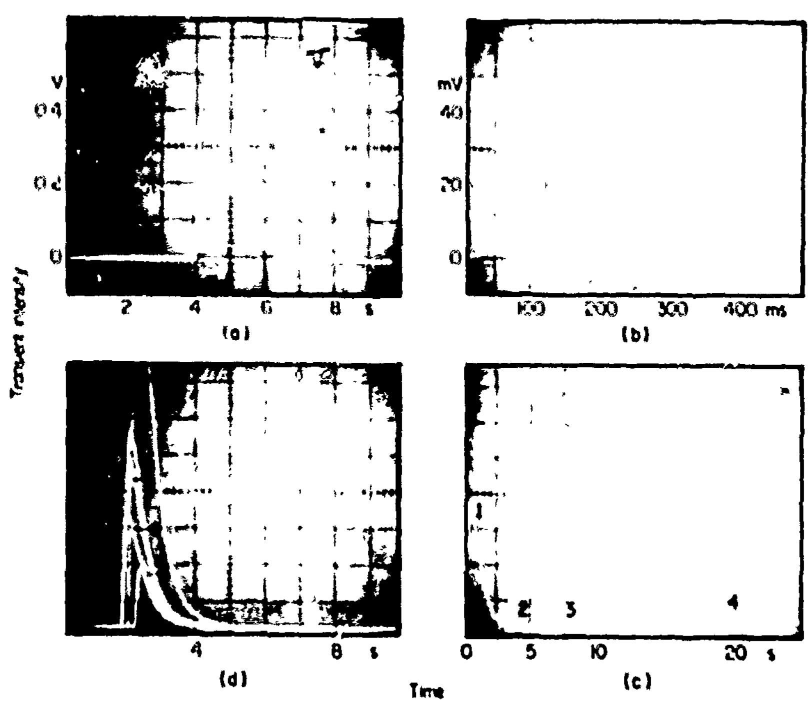

Fig. 3. Oscilloscope trace recordings illustrating the time profiles of flash-initiated increases in the mass spectrometer ion count at *m/e* 32 and attributed to oxygen released into the gas phase from ZnO surfaces due to photolysis: (a) oxygen transient from the first flash incident via a quartz envelope onto a well-outgassed ZnO sample at a residual system pressure of 10^{-6} N m^{-2}; (b) initial rise and decay of the oxygen transient generated by the first flash incident through a Kodial glass envelope; (c) time sequence illustrating lack of reproducibility in transient size for four flashes delivered at ca. 5 s intervals through Kodial glass; (d) progressive decrease in oxygen transient for five flashes incident at 20 s intervals through quartz.

at m/e 32 initiated by the single flash followed by a slower decrease back to the pre-flash level when observed on a time scale of 1 s/div. No such transient was observed at the m/e value for zinc vapour or any other m/e values — except those for 'system' transients (see below). Figure 3(b) demonstrates the rise in ion current at m/e 32 on a much faster time scan (20 ms/div.). Comparison with output of the flash-tube, as monitored by a photodiode and displayed simultaneously on the second trace of the storage 'scope', confirmed that the slow rise evident in Fig. 3(b) did not originate in the lamp pulse but originated from time-of-diffusion from the flash reactor to the mass spectrometer. The slow decay of signal intensity at m/e 32 after the pulse, evident in Fig. 3(a), originates from the pump-down rate of the ion-pump. The over-all shape of the initial pressure rise and subsequent decrease resembles that reported from thermal desorption studies with subsequent readsorption.[11] Application of the kinetic analysis developed by previous workers, with insertion of appropriate rates of pumping by the ion pump and measured rates of pressure increase caused by the flash, indicated that the maximum reached in traces such as Fig. 3(a) is a good approximation (within 10%) to the true maximum which would be attained in the absence of continuous pumping by the ion pump. The latter condition was not normally used in the present study, to avoid possible evolution of contaminants when the ion pump was switched off. The maximum reached ca. 200 ms after the flash for transients such as that shown in Fig. 3(a) and measured under continuous pumping is taken as a good approximation to the actual pressure increases and as providing a good measure of the relative magnitudes of transients in various conditions and from various samples. Observed signal heights were converted to 'equivalent pressure increases' by calibration of the mass spectrometer sensitivity with known pressures of oxygen.

When light was incident through Kodial glass onto titanium dioxide/quartz samples in vacuum of 10^{-6} N m^{-2}, no transient comparable in intensity or behaviour to that illustrated in Fig. 3 was detected, despite care taken to prepare, thermally treat and flash-illuminate the titanium dioxide samples in conditions identical to those used for zinc oxide. With photons incident through a quartz envelope, a small transient at m/e 32 was sometimes detectable from fresh titanium dioxide/quartz samples but it was lower by a factor of 50 than the transient observed from a similarly treated zinc oxide sample. Data on relative pressure increases are summarized in Table 2, column 3. These demonstrate that oxygen evolution from zinc oxide surface *in vacuo* was much more efficient than from titanium dioxide surfaces. The marked difference between extent of oxygen evolution from zinc oxide and titanium dioxide provides support for our view that the observed effect at m/e 32 depended on specific interaction of the light flash with the metal-oxide samples, rather than with the system.

If traces such as Fig. 3(a) originated solely from photolysis of the zinc oxide surface with release of oxygen, similar yields of oxygen might be expected from successive pulses. Photographs (c) and (d) of Fig. 3 demonstrate, however, that magnitude of flash-initiated transients monitored at m/e 32 decreased progressively to a limiting value when successive flashes were delivered to the same zinc oxide surface at short intervals. However, if the flash-illuminated zinc oxide surface was kept in the dark for an hour or longer between two sequences of flashes, behaviour similar to that shown in Fig. 3(d) could be repeated. A possible interpretation of this behaviour was that the zinc oxide surface slowly acquired a saturation coverage of depletively chemisorbed oxygen in the dark by interaction with residual oxygen pressure (which was not measurable but $<10^{-6}$ N m^{-2}). Flash-initiated desorption of much of this chemisorbed oxygen might then account for the observed high transient at m/e 32 by the first flash delivered after standing in the dark for times of at least one hour. The lower yield shown in Fig. 3(d) for subsequent flashes delivered to zinc oxide surfaces at 1 min intervals might also be understood on this basis, since a 1 min delay between pulses would not suffice to restore saturation coverage by O_2^- at oxygen pressures $<10^{-6}$ N m^{-2}.

The wavelength dependence of oxygen evolution from zinc oxide *in vacuo* was studied in an attempt to determine whether the variable flash-initiated oxygen evolution originated from photolysis of surface regions of zinc oxide or from photodesorption of oxygen re-adsorbed between flashes. The literature provided some basis for attempting thus to discriminate between the two processes, since photolysis has been associated only with photons inside the band edge at 380 nm (and usually with photons of $\lambda<365$ nm), whereas oxygen photodesorption had been reported at wavelengths outside the band edge[6] (and as far as $\lambda\sim500$ nm). A Wratten

Table 2. Magnitude of flash-initiated oxygen transients from zinc oxide and titanium dioxide.

Steady state oxygen pressure	Metal oxide	Initial rapid effect[a]		Slow secondary process[b]	
P_{O_2}/Nm^{-2}		ΔP_{O_2}/Nm^{-2}	$\phi_{p.d.}$[c]	ΔP_{O_2}/Nm^{-2}	ϕ_{pox}[d]
(a) Flash incident through quartz (λ > 200 nm)					
< 3×10^{-4}	ZnO-SP500	$+1 \times 10^{-4}$	5×10^{-3}	-	-
< 3×10^{-4}	TiO_2	$+2 \times 10^{-7}$	< 10^{-7}	-	-
1×10^{-3}	"	$+6 \times 10^{-3}$	3×10^{-3}	4×10^{-3}	2×10^{-3}
8×10^{-3}	"	$+6 \times 10^{-3}$	3×10^{-3}	-4×10^{-3}	2×10^{-3}
(b) Flash filtered by WR 38A (λ > 360)					
< 3×10^{-4}	ZnO-SP500	10^{-7}	-	-	-
1×10^{-3}	"	$+1 \times 10^{-3}$	~ 10^{-3}	-	-
4×10^{-3}	"	"	"	-	-
9×10^{-3}	"	"	"	-	-
< 3×10^{-4}	TiO_2	-	-	-	-
2×10^{-3}	"	$+3 \times 10^{-3}$	3×10^{-3}	~ 10^{-3}	~10^{-3}
4×10^{-3}	"	"	"	"	"
6×10^{-3}	"	"	"	"	"

[a] Corresponds to photodesorption or photodecomposition of the solid with $t_{1/2}$ ca. 150 ms.
[b] Corresponds to photo-oxidation of the titanium dioxide surface occurring at times 2—20 s.
[c] ϕ_{pd} is the quantum efficiency of photodesorption.
[d] ϕ_{pox} is the quantum efficiency of photo-oxidation.

38A filter offered the possibility of transmitting a significant fraction of photons active for photodesorption but very few photons active for photolysis, since it transmitted significantly (>1%) only in the wavelength range 360—620 nm. Using a potassium ferrioxalate actinometer, it was possible to determine that the number of photons expected to be active for photodesorption (λ < 500 nm) which were incident through the 38A filter and quartz windows was 6×10^{17} per flash. No measurable flash-initiated oxygen evolution was observed for zinc oxide surfaces *in vacuo* for this photon flux incident through the filter. The total flux at 200—500 nm incident through quartz without the 38 A filter was measured as 54×10^{17} photons per flash. Although this represented only a ninefold increase in intensity of light which would be active for oxygen photodesorption, oxygen evolution was enhanced to a much greater extent (at least fiftyfold, allowing for the experimental signal-to-noise ratio). It appeared from this extra enhancement that photolysis by photons at 200—360 nm made the major contribution to flash-initiated oxygen evolution from zinc oxide for photons incident through quartz. Since these experiments showed that use of the 38A filter effectively suppressed contributions by such photolysis, this filter provided a convenient method for studying photosorption processes without interference by photolysis. Data in this latter conditon are presented in the following section.

Oxygen photosorption processes at O_2/ZnO *and* O_2/TiO *interfaces*

O_2/ZnO. Figure 4 reproduces photographs of oscilloscope trace recordings which demonstrate flash-initiated release of molecular oxygen from an O_2/ZnO interface under three oxygen pressures. As illustrated in photograph (d) of this figure, flash-initiated enhancement of oxygen pressure had a rise time of 200 ms at each pressure. Figure 4(a) demonstrates that at an oxygen pressure of 10^{-3} N m^{-2}, the peak height of the transient was 10 ± 2 mV for a sequence of five flashes delivered at 1 min intervals. This extent of reproducibility contrasts markedly with the lack of reproducibility for evolution of photolytic oxygen from similar zinc oxide surfaces when maintained in vacuum of 10^{-6} N m^{-2} and flash-illuminated without use of the Wratten 38A filter (compare Fig. 4(a) with Fig. 3(d)). Hereinafter, any reproducible flash-initiated release of molecular oxygen from zinc oxide or titanium dioxide shall be referred to

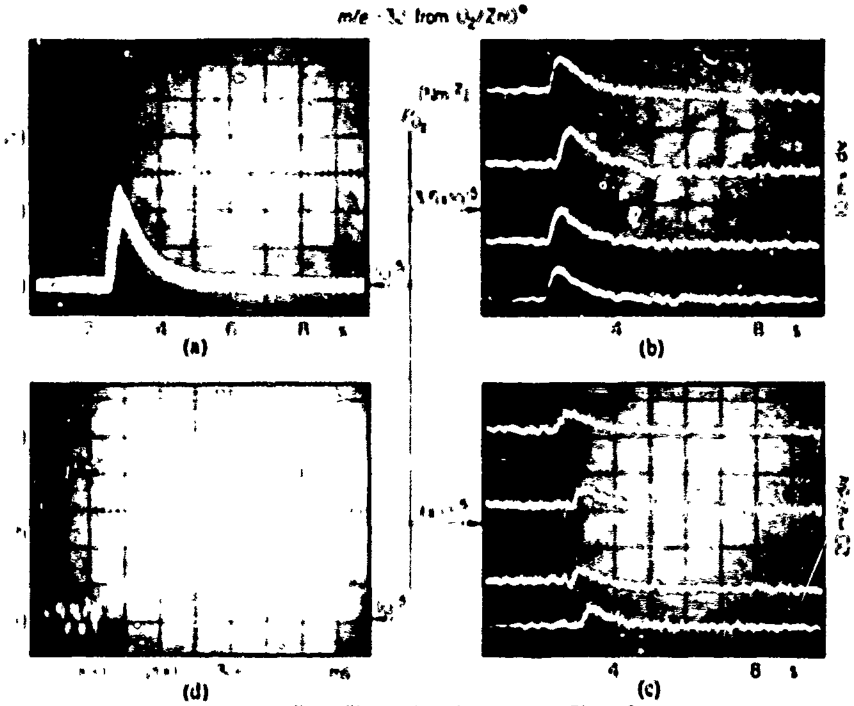

Fig. 4. Oscilloscope trace recordings illustrating the time profiles of transients produced by the photodesorption of oxygen from ZnO/O_2 interfaces under the indicated pressures of oxygen. In all cases the light pulses were incident via a Wratten 38A filter and transients were monitored at *m/e* 32. (a) Superposition of five oscilloscope traces for five successive pulses delivered at 60 s intervals with an oxygen pressure of 10^{-5} N m^{-2} (sensitivity 5 mV/div.) (b) Four traces illustrating reproducibility of oxygen photodesorption at system pressure 3.5 × 10^{-4}N m^{-2} (sensitivity 10 mV/div). (c) Four traces illustrating the reproducibility of oxygen photodesorption at a system pressure of 9 × 10^{-4}N m^{-2} sensitivity 20 mV/div). (d) Initial rise of the flash-initiated transient attributable to oxygen photodesorption at a system pressure of 10^{-6}N m^{-2} (sensitivity 2 mV/div).

as photodesorption if measured in conditions which render insignificant any contributions from photolytic oxygen.

Figure 4(b) and Fig. 4(c) demonstrate that magnitude of flash-initiated photodesorption by photons transmitted through filter 38A did not increase significantly when steady state oxygen pressure was increased sixfold to 9 × 10^{-4} N m^{-2}. These photographs demonstrate again the reproducibility of peak heights for flashes delivered at 1 min intervals but, in addition, they illustrate an experimental limitation, viz. that as steady state oxygen pressure increased, it became necessary to operate the detection system at progressively less sensitive settings. This effectively limited study of the small oxygen photodesorption peak of O_2/ZnO* to pressures <10^{-4} N m^{-2} with the available detection equipment. This limitation will be removed in future studies by use of an electronic unit to 'back-off' the ion signal at *m/e* 32 and so permit detection of transients on sensitive ranges at oxygen pressures up to ca. 10^{-2} N m^{-2}. The data in Fig. 4 indicate, however, that oxygen photodesorption is effectively independent of pressure at steady state oxygen pressures in the range 10^{-6}—10^{-4} N m^{-2}. This in turn suggests that only a limited number of sites existed on the zinc oxide surface which were able to yield oxygen by photodesorption under flash illumination by light transmitted through Wratten 38A filter. Limitations imposed by boundary layer theories on the surface concentrations of O_2^- may be important factors limiting the efficiency of oxygen photodesorption to the low values listed in Table 2, column 4. These approximate values were obtained by using a potassium ferrioxalate actinometer to measure the number of 360—500 nm photons transmitted through the Wratten 38A filter with geometry identical with that used for the photodesorption studies, except that the actinometer cell replaced the metal oxide/quartz sample. Total oxygen photodesorption was obtained by multiplying the height of the observed transient at *m/e* 32 by an oxygen sensitivity factor experimentally determined for the mass spectrometer, and by the system volume. Quantum efficiencies of photodesorption (ϕ_{pd}) obtained from the ratio of these two numbers are probably too low by a factor ca. 2, since the white zinc oxide or titanium dioxide surfaces reflected many of the 400-500 nm range photons which potassium ferrioxalate solutions absorbed. Measurements with another Wratten gelatin filter (No. 40 transmitting 450—700 nm and also in the near IR) confirmed this point since the photon flux was approximately halved but no oxygen photodesorption was detectable despite the presence of 450—500 nm photons. The negative photodesorption result with this Wratten 40 filter confirmed the importance of 360—450 nm photons for oxygen photodesorption and also discounted the possibility that transients such as those in Fig. 4 originated from surface heating in the flash. It thus appears that the data in Table 2, column 3 represent true oxygen photodesorption and that the quantum efficiencies there listed are within an order of magnitude of the true value. They characterize oxygen photodesorption as a highly inefficient process when initiated by ca. 6×10^{17} photons in the wavelength range 360—450 nm delivered as a pulse of 50 μs duration to O_2/ZnO interfaces at steady state oxygen pressures of 10^{-5}—10^{-4} N m^{-2}.

O_2/TiO_2. Flash illumination of O_2/TiO_2 systems through filter 38 A resulted in time profiles of the types illustrated in Fig. 5(a). These flash-initiated transients indicate an initial small increase ($2.5 \pm 1.0 \times 10^{-6}$ N m^{-2}) of oxygen pressure reaching its maximum ca. 0.5 s after the flash. The pressure decrease at times 0.5—2 s after the flash apparently carried the system pressure to values slightly lower ($1.5 \pm 1.0 \times 10^{-6}$ N m^{-2}) than the steady state level prior to the flash. Within the indicated limits on reproducibility neither the initial rapid increase nor the subsequent persistent decrease was markedly dependent on oxygen pressure in the range 10^{-5}—10^{-4} N m^{-2} when light was incident through the 38A filter.

Removal of the 38A filter, so that 54×10^{17} photons in the wavelength range 200—500 nm became incident through a quartz window onto the O_2/TiO_2 interface, resulted in much larger transients which took the form shown in Fig. 5(b) at 10^{-4} N m^{-2} steady state oxygen pressure. The time profile of this transient reveals much more clearly than that of Fig. 5(a) the dual nature of the flash-initiated transient at *m/e* 32: an initial rapid pressure increase of 6×10^{-6} N m^{-2} is succeeded by decay at 2 s to a pressure lowered by the same amount relative to the pre-flash steady state oxygen pressure. Persistence of reduced pressure is still evident at 8 s after the flash. Such time profiles were fully reproducible for a short sequence of flashes delivered at 1 min intervals at each fixed steady state pressure of oxygen. Varying this pressure altered the relative magnitudes of the flash-initiated rapid increase and slower more persistent decrease (compare Fig. 5b and Fig. 5c). Data on these effects are collected in Table 2 and expressed in column 4 as apparent quantum efficiencies for photodesorption, ϕ_{pd}, (based on the initial pressure increase), or in column 6 as ϕ_{pox}, the quantum efficiency for flash-initiated oxidation of the titanium dioxide surface (based on the persistent reduction of oxygen pressure). Photo-oxidation is preferred to photoadsorption as the mechanism responsible for photoinitiated decrease in oxygen pressure, because uptake of oxygen by the illuminated titanium dioxide surface was effectively irreversible.

This was established by parallel experiments in which the oxygen uptake at the O_2/TiO_2 interface was monitored during illumination on a sealed glass high vacuum system and the oxygen pressure was monitored for some hours after illumination. These measurements showed that oxygen taken up from the gas phase during illumination was not released in the dark but was irreversibly incorporated into the titanium dioxide sample under UV illumination. Surface photo-oxidation is thus a more appropriate description of the photoassisted oxygen uptake. On this interpretation, the pressure decreases evidence in Fig. 5 at times 2—8 s after a flash correspond to the ϕ_{pox} values listed in column 6 of Table 2.

Present results on flash-initiated transients in the O_2/TiO_2 system illustrate one major advantage of the dynamic fast-detection system, viz. the capability of time-resolving the opposing processes of rapid photodesorption and slower photo-oxidation. Since most previous studies of oxygen photosorption relied on slow-response techniques and continuous low-intensity illumination, it is hardly surprising that net evolution of oxygen has been reported as the dominant process in some conditions, whereas other researchers report net uptake of oxygen in different conditions.[8] The time-resolution illustrated in Fig. 5 should make it possible in future work on titanium dioxide to determine which conditions favour photodesorption and which enhance surface photo-oxidation.

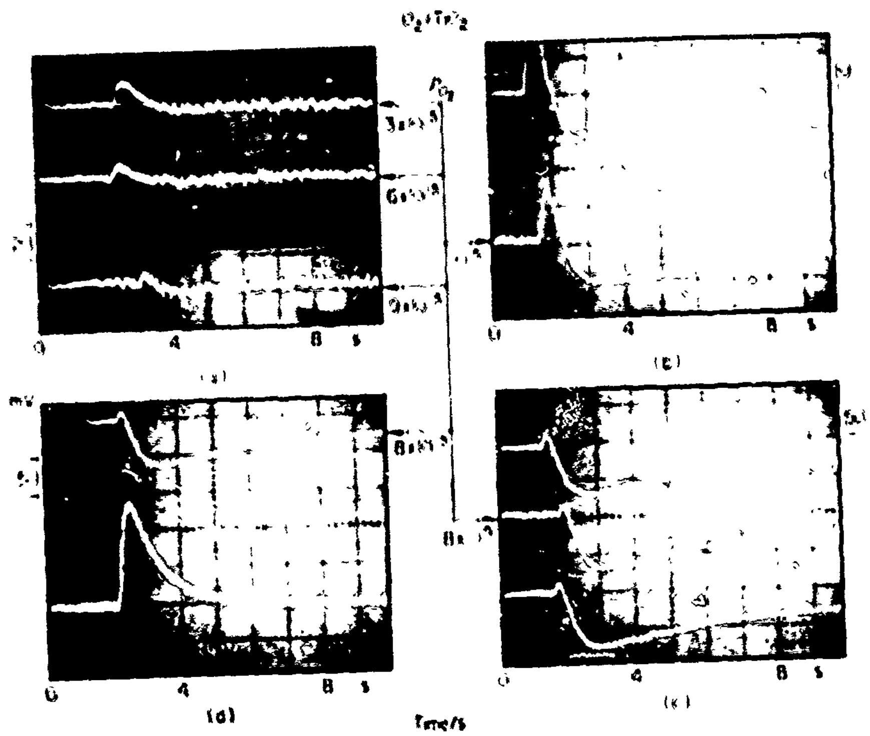

Fig. 5. Oscilloscope trace recordings showing time profiles of flash-initiated oxygen transients at *m/e* 32 above TiO_2 surfaces with indicated pressure of oxygen (N m^{-2}): (a) transient time profile at 20 mV/div under three indicated oxygen pressures for light incident through a Wratten 38A filter; (b) transient time profile at 10 mV/div for two flashes incident through the quartz envelope; (c) reproducible time profiles for light incident via quartz with an oxygen pressure of 8×10^{-5} N m^{-2}; (d) time profile at *m/e* 32 (upper trace) contrasted with profile at *m/e* 29 (lower trace).

Discussion of oxygen photoeffects

The results described above demonstrate conclusively that much greater photolysis occurred at 'fresh' zinc oxide surfaces than at fresh or aged titanium dioxide surfaces when flash illuminated in vacuum of 10^{-6} N m^{-2}. The progressive large decline in the extent of zinc oxide photolysis noted for flashes delivered at short (1 min) intervals could be attributed *either* to an inhibiting effect of excess zinc built up at the surface by photolysis[14,15] *or* to the need for longer recovery times to re-establish equilibrium band-bending after each flash. The latter explanation appears to be more probable in view of the observation that oxygen transients generated at 1 min intervals were much more reproducible in the presence of 10^{-4} N m^{-2} of gaseous oxygen (cf. Fig. 4). Rapid chemisorption of oxygen after each flash would contribute to rapid restoration of equilibrium band-bending. Absence of significant photolysis of titanium dioxide facilitated observations of the post-flash depletion of oxygen from the gas phase which persisted for up to 20 s. Since a collision rate of ca. 3×10^{16} s^{-1} would be calculated for oxygen molecules with the geometric area of the flash illuminated TiO_2 sample, whereas a net number of 5 × 10^{17} paramagnetic surface Ti^{3+} centres are readily attainable for the titanium dioxide used,[illegible] the long depletion times are readily explicable as the time needed for gas-phase oxygen to collide and react with Ti^{3+} centres created by the flash. Very slow post-flash restoration of electronic equilibrium at TiO_2 surfaces is also consistent with reportedly low electronic mobilities.[illegible]

3. Photoeffects Involving Molecules Other Than Oxygen

A. INTRODUCTION

In the above considerations of photoeffects at O_2/ZnO^* and O_2/TiO_2^* interfaces, it became clear that important parameters were the number and sign of charged species present at these interfaces. Chemisorption of various molecules onto zinc oxide or titanium dioxide may (i) leave these parameters unaffected (*weak* chemisorption); (ii) increase the extent of negative charge on the surface and so deplete the number of electrons mobile in the conduction band of the solid (*depletive* chemisorption); or (iii) increase the amount of positive charge on the surface and so increase the number of electrons in the conduction band (*cumulative* chemisorption). Depletively chemisorbed molecules might be expected to exhibit photodesorption effects similar to those noted for oxygen. Photoeffects different both in kind and in magnitude from those noted with oxygen might be expected for molecules which experience weak or cumulative chemisorption on zinc oxide or titantium dioxide. Detailed information on the form of chemisorption exhibited by various molecules on zinc oxide and titanium dioxide at room temperature was, therefore, most desirable in selecting molecules likely to exhibit photosorption, photocatalysis or photoassisted reaction under flash illumination. Such information is available in the literature concerning very few molecules and reports by various workers do not always agree. Chemisorption of hydrogen onto zinc oxide is a case in point, since some reports claim that hydrogen does not chemisorb onto zinc oxide at room temperature[illegible] but other workers[illegible] espouse several forms of chemisorption.

Despite criticisms by some workers,[illegible] techniques involving measured changes in the electrical conductivity of zinc oxide and titanium dioxide when gases adsorb have been extensively used as a convenient indicator as to whether various molecules experience weak, cumulative or depletive chemisorption. On the basis of this criterion, there is fairly general agreement that hydrogen experiences cumulative chemisorption. On balance, available conductivity data[illegible] indicate that ethanol molecules, like hydrogen, experience cumulative chemisorption on zinc oxide, although the relative proportions of dissociative and non-dissociative chemisorption are not clear. Consequently, the interfaces H_2/ZnO and C_2H_5OH/ZnO represent a pair likely to carry excess positive surface charge as a result of chemisorption in the dark. Figure 1(b) should then accurately describe these interfaces in collective-electron terms. The downward bending of bands near these interfaces should favour migration of photogenerated holes towards the interior of zinc oxide and of electrons towards the interface. This is the converse to processes at O_2/ZnO^* interfaces. Consequently, differences both in kinetics and in efficiency of photoeffects (e.g. photosorption processes) are to be expected between these systems and the O_2/ZnO^* system. The literature on photoeffects in H_2/ZnO^* is limited to reports that hydrogen experiences photoadsorption and photoassisted H/D exchanges[illegible] over zinc oxide under continuous illumination and to observations that pre-adsorbed oxygen or hydrocarbons give rise to additional apparent photoadsorption.[illegible] Reported studies of photoeffects in ethanol/zinc oxide systems have mainly dealt with the high reactivity of the ethanol molecules towards photogenerated holes[illegible] and have largely been carried out with zinc oxide in contact with aqueous phases containing ethanol. It is clear from these studies that, for illuminated C_2H_5OH/ZnO^* interfaces, photoassisted oxidation of ethanol molecules must be taken into consideration as well as possibilities for photosorption.

Conflicting claims have been made, based on electrical conductivity data, on the nature of adsorption of carbon monoxide or water onto zinc oxide. Older reports[1] generally refer to carbon monoxide experiencing cumulative chemisorption similar to hydrogen but it has recently been claimed[illegible] for clean zinc oxide surfaces that carbon monoxide experiences depletive chemisorption detectable even at 10^{-4} N m^{-2} pressure of carbon monoxide. If these latter reports are correct, then CO/ZnO^* systems could be expected to exhibit photodesorption similar to that reported here for O_2/ZnO^*.

Published research from the authors' laboratories have shown that some polyatomic gas molecules which exhibit depletive chemisorption on zinc oxide, viz. nitrous oxide, methyl iodide-d, and methyl chloride undergo photoassisted gas/solid reactions.[14,15] Thus nitrous oxide experiences photoassisted dissociation mainly to the product N_2, while adsorbed O^- fragment ions remain and negatively bias the N_2O/ZnO interface. Contributions by hydrogen-containing surface sites to a net photoassisted reaction was demonstrated by predominance of CD_3H (and CD_4) in the methane product from photoassisted reaction between CD_3I and UV illuminated zinc oxide.[16] The results correlated well with IR studies of surface hydroxyl concentration.[16] Stone has recently correlated the activity of titanium dioxide surfaces with the hydroxyl concentration[17] and the influence of hydroxyls and of adsorbed water has been studied by photoconductivity and thermogravimetric techniques.[18,19]

Some information is also available on the nature of adsorption and photoeffects experienced by simple hydrocarbons over illuminated zinc oxide and titanium dioxide. For methane and ethane, slow activated chemisorption has been reported in the dark, and photoadsorption is reported for methane. Differing surface heterogeneities in various samples may be responsible for apparently conflicting claims concerning ethylene adsorption on zinc oxide, which Kokes *et al.* claim to be rapid and reversible, while other workers exclude ethylene from lists[21] of molecules experiencing rapid chemisorption or attribute[22] irreversible poisoning effects to C_2H_4. Selective photocatalysed partial oxidation of butanes to aldehydes and ketones has been well documented over titanium dioxide, which also exhances oxidation of ethylene and propylene.

B. EXPERIMENTAL

The dynamic mass spectrometer system was utilized in a similar manner to that employed for studying oxygen transients, except that transients were monitored at each integral *m/e* value—usually between 1 and 50 at 4 MHz r.f. It soon became apparent that meaningful study of transients at *m/e* 44, 28, 18, 16 or 12 was not possible using quartz or Kodial envelopes because peaks similar to those shown in Fig. 6 occurred at these *m/e* values regardless of what sample was present in the system. These transients corresponded to flash-initiated increases of gas phase components in the high-vacuum system with these *m/e* values. Transients of similar time profiles but reduced peak height occurred even when no metal oxide or gas was present and the system pressure was $<10^{-6}$ N m^{-2}. For obvious reasons, they are termed 'system transients' and are attributed to flash-initiated desorption of carbon oxides and water from internal surfaces of the vacuum system. With the metal oxide/quartz samples in position, these 'system transients' were largest for light incident via a quartz window, smaller by factors ca. 0.1 with a Kodial window and absent (with the exception of *m/e* 28, 16 and 12) when either the quartz or Kodial window was wrapped around with a appropriate gelatine filter (Wratten 38A) which excluded most UV and IR photons. Parallel behaviour of system transients at *m/e* 28, 16 and 12 supported their assignment to carbon monoxide. Since this was a major component of residual gases in the stainless steel high-vacuum system, presence of a carbon monoxide transient was hardly surprising.

Possible photosorption effects involving

$$^{13}C^{18}O_2,\quad ^{15}N_2{}^{18}O,\quad ^{15}N_2,\quad ^{13}C^{18}O,\quad H_2{}^{18}O \quad \text{or} \quad ^{13}CH_4$$

were, however, excluded from meaningful study using Kodial or quartz windows, owing to the coincidence of their major ion fragments with the system transients. Photosorption and other photoeffects could, however, be studied by selecting molecules whose major ion fragments did not coincide with system transient, e.g.

$$H_2,\quad D_2,\quad ^{14}N^{15}N^{18}O,\quad C_2H_5OH \quad \text{or} \quad C_2D_5OD$$

The procedure involved establishing a steady state pressure, ca. 10^{-6}—10^{-3} N m^{-2}, of the chosen gas over the zinc oxide or titanium dioxide surface as a dynamic balance between gas admission through a variable leak valve and removal by the ion pump. With the mass spectrometer manually set to the peak of an appropriate major ion fragment, (e.g. *m/e* 45, 31, 29 from $^{15}N^{15}N^{16}O$), time profiles were recorded for flash-initiated changes in ion current from their steady state values. Since the resolution of the mass spectrometer was not constant across the *m/e* range 1—50, resolution settings were chosen to ensure '>5% valley' resolution between adjacent peaks for the *m/e* range of maximum interest for each gas (e.g. resolution was optimized over the region *m/e* 50—25 for study of $^{15}N^{15}N^{16}O$).

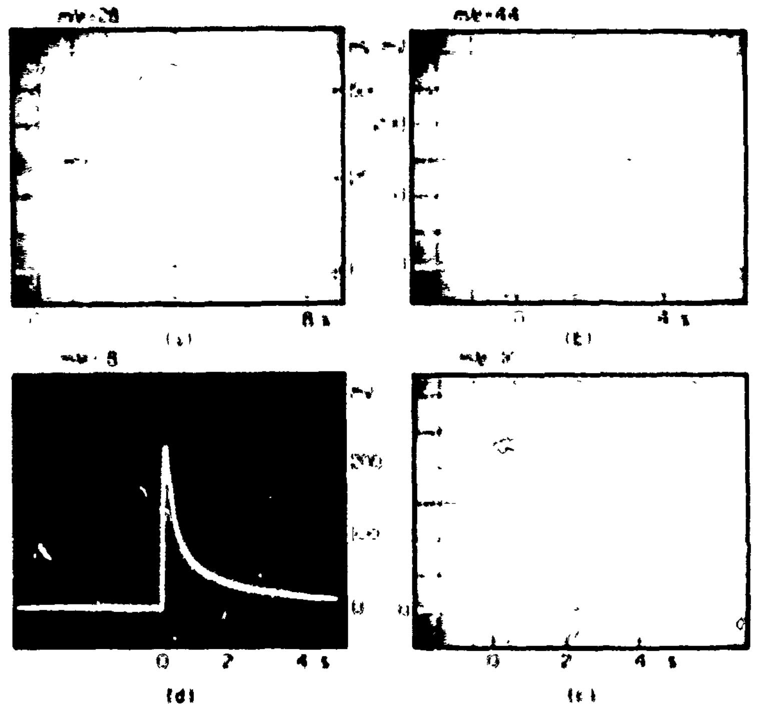

Fig. 6. Oscilloscope trace recordings illustrating the time profiles of 'system transients' monitored at *m/e* values corresponding to CO^+, CO_2^+, O^+ and H_2O^+. The transients shown here were initiated by pulses incident via a quartz envelope with a zinc oxide sample in position. Similar but smaller transients were observed if the zinc oxide sample was removed.

C. RESULTS

Flash-initiated transients in systems exhibiting depletive chemisorption

Results of previously published studies with low-intensity long-duration UV illumination incident on N_2O/ZnO^* interfaces had led to the conclusion that photoassisted conversion to $N_2(g)$ and $O^-(ads)$ was important at this interface.[14] The existence of system transients at *m/e* 44, 28, 16, 14 and 12 effectively prevented meaningful study of photoassisted conversion of normal N_2O to $N_2 + 1/2\,O_2$. Use of $^{15}N^{15}N^{16}O$ lifted the coincidence of parent and fragment ions with system transients at *m/e* 44 and 28 and allowed the parent ions of nitrous oxide at *m/e* 45 ($\equiv ^{15}N^{15}N^{16}O^+$), or of nitrogen products at *m/e* 29 ($\equiv ^{15}N^{15}N^+$), to be studied without interference from system transients. Figure 7 demonstrates that opposite transient effects were observed when identical flashes were incident on $^{15}N^{15}N^{16}O/ZnO$ and changes were monitored at *m/e* 45 or 29, respectively. For these experiments $^{15}N^{15}N^{16}O$ was flowing at room temperature at a steady state pressure of 8×10^{-5}N m^{-2} over a zinc oxide surface previously baked out *in vacuo* ($\sim 10^{-4}$ N m^{-2}) for 48 h at 350°C. The upper trace of Fig. 7(b) demonstrates a flash-initiated *decrease* in signal level at *m/e* 45, consistent with photoassisted depletion of nitrous oxide pressure, P_{N_2O}. This depletion persisted for times greater than 8 s after the flash. The lower trace demonstrates exactly converse flash-initiated behaviour for ions with *m/e* 29, as would be expected if photoassisted depletion of $^{14}N^{15}N^{16}O$ resulted in formation of $^{14}N^{15}N$ according to eq. (5)

$$^{14}N^{15}N^{16}O + h\nu \rightarrow {}^{14}N^{15}N + 1/2\, O_2 \qquad (5)$$

Resolution was better than "5% valley" between adjacent peaks and no comparable transients were observed from fresh zinc oxide surfaces at *m/e* 45, 29 or 31 when the zinc oxide substrate was flash-illuminated through quartz prior to exposure to $^{14}N^{15}N^{16}O$. Further confirmation that the effects shown in Fig. 7(b) were real and characteristic of the illuminated $^{14}N^{15}NO$/ZnO* interface, rather than experimental artifacts, came from the observation that carrying out an identical set of procedures for light incident on $^{14}N^{15}N^{16}O$/TiO_2* interfaces did *not* yield any such transients. This was in agreement with previous reports[illegible] that photoassisted dissociation of nitrous oxide does not occur over titanium dioxide and it demonstrated conclusively that the transients did not originate from the vacuum system or from direct photolysis of the $^{14}N^{15}N^{16}O$.

A point of interest for the flash-illuminated $^{14}N^{15}N^{16}O$/ZnO* system was the question of whether or not oxygen remained adsorbed on the zinc oxide in accordance with the stoichiometry of eq. (5). Flash illumination through the quartz envelope did not permit unequivocal answers to this question, because the oxygen transient from photolysis of the zinc oxide surface swamped any small additional oxygen, such as would be equivalent to the $^{14}N^{15}N$ detected. Table 2 illustrated that use of a Wratten 38A filter reduced to zero any oxygen transient at *m/e* 32 from photolysis of zinc oxide and new tests confirmed that no flash-initiated transient at *m/e* 32 was detected with this filter in position either from a 'fresh' zinc oxide surface or from the $^{14}N^{15}N^{16}O$/ZnO system in steady state conditions. However, when flashes became incident through this filter onto a zinc oxide surface *previously* flash illuminated through quartz with $^{14}N^{15}N^{16}O$ present, a readily measurable transient was detected at *m/e* 32. This oxygen transient is attributed to oxygen produced at the N_2O/ZnO* interface during flash illumination and later photodesorbed by light incident through the Wratten 38A filter. These observations lend further support to the view that dissociation did occur according to (5) in the N_2O/ZnO* system.

Another photolytic pathway which merited study for the $^{14}N^{15}N^{16}O$ system is indicated by eq. (6) which corresponds to bimolecular head-to-head interaction:

$$^{14}N^{15}N^{16}O(g) \rightleftharpoons {}^{14}N^{15}N^{16}O(ads) \xrightarrow[h\nu/ZnO]{+\,^{14}N^{15}N^{16}O} {}^{14}N_2 + 2(^{15}N^{16}O)(g) \qquad (6)$$

An important role had been suggested for O^- in initiating reactions similar to (7) in previous studies.[illegible] Since formation of this species has also been suggested on zinc oxide surfaces, occurrence of (7) appeared possible and should lead to $^{15}N^{16}O$. Flash-initiated transients at *m/e* 31 were therefore examined. Bearing in mind that ion fragments from $(^{14}N^{15}N^{16}O)^+$ contribute to ion signals with *m/e* 31, together with parent ions from possible $^{15}N^{16}O$ products, it was to be expected that this ion signal should demonstrate more complex flash-initiated behaviour than that of N_2O^+ or N_2^+. Such complex behaviour is illustrated in Fig. 7(c), where it may be noted that an initial flash-initiated increase in signal level occurred from the steady state value at times ca. 200 ms after the flash, but that this was later succeeded by a slower decay to values below the pre-flash level at times between 1 s and 8 s after the flash. This latter slow decrease is consistent with, and has a similar time profile to, the long persistence of flash-initiated depletion of $P(^{14}N^{15}N^{16}O)$ after the flash, which is illustrated in Fig. 7(b). A different process must, however, be responsible for the initial rapid increase in ion current evident in Fig. 7(c) at times ca. 200 ms after the flash. Fast photodesorption of the $^{15}N^{16}O$ product

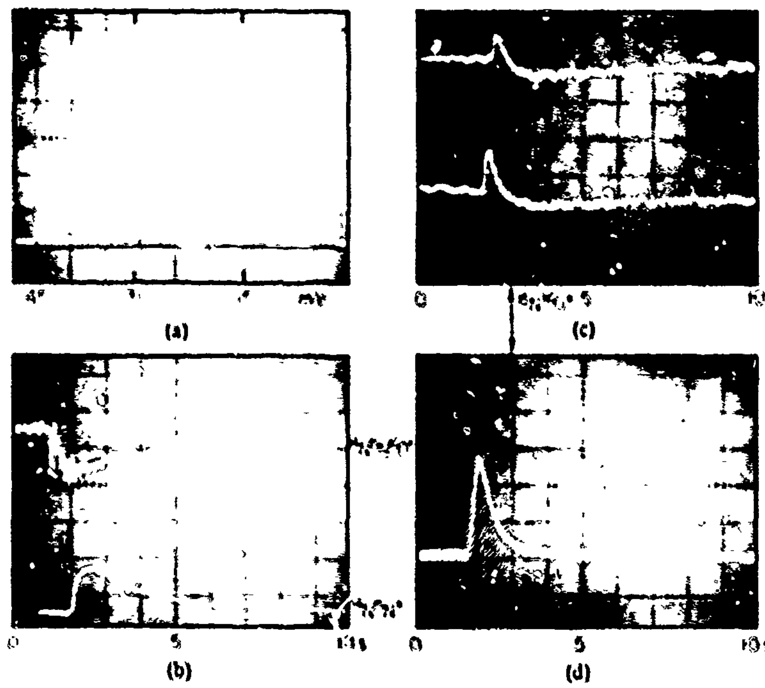

Fig. 7. Oscilloscope trace recordings of mass spectral measurements on ''N''N''O/ZnO systems. (a) Mass spectrum of ''N''N''O gas before contact with ZnO. Spectrum run at identical settings to those used for (b), (c) and (d). (b) Upper trace: time profile, monitored at a sensitivity of 10 mV·div, of the flash-initiated decrease in ion current at *m/e* 45, (''N''N''O⁺) combined with the time profile (lower trace) of the flash-initiated increase in ion current at *m/e* 29 (''N''N⁺) monitored at the same sensitivity. The pulses were incident onto an N_2O/ZnO interface at a pressure of 8 × 10'N m'. (c) Time profile of flash-initiated changes in the ion current monitored with a sensitivity of 5 mV·div at *m/e* 31 (corresponding to ''N''O⁺) for light incident onto the N_2O/ZnO interface at a pressure of 8 × 10'N m'. (d) Time profile of flash-initiated transient from same ZnO surface as used in (c) except that the gas-phase N_2O was pumped away from the previously flash-illuminated surface prior to this flash.

formed via (6) was suspected and, since published ESR work[3] indicated that nitric oxide chemisorbs onto the surface of zinc oxide, it appeared possible that some fraction of any ''N''O so produced might remain on the zinc oxide surface after flash illumination. This possibility was tested by pumping away all gas-phase nitrous oxide and then looking for a flash-initiated transient at *m/e* 31. Figure 7(d) illustrate the time profile of the flash-initiated transient then observed. No such transient at *m/e* 31 was observed from zinc oxide surfaces prior to exposure to ''N''N''O. Comparison of Fig. 7(c) with Fig. 7(d) confirms that the fast initial increase in ion current at *m/e* 31 had a similar time profile with or without gas-phase ''N''N''O present during the flash. This is consistent with assignment of this 'fast' component of the transient to photodesportion of ''N''O from surfaces were it was formed by reaction of ''N''N''O with flash illuminated zinc oxide.

The system CD_3I/Zno was briefly investigated as another example of one exhibiting depletive chemisorption.[6] Since methyl iodide-d_3 adversely affected the electron multiplier, the flow of reactant methyl iodide-d_3 over the zinc oxide catlayst surface was trapped by a liquid nitrogen cooled baffle (LNB in Fig. 2), so that only products not condensable at 77 K would be passed to the mass spectrometer for analysis and detection. According to previous results, methane-d_4 should be one such product, but flash illuminatin of CD_3I/ZnO* in these conditions did not yield a transient at *m/e* 20. However, a readily measurable transient was detected at *m/e* 19, indicating flash-initiated production of CD_3H over the CD_3I/ZnO interface. This result resembles that obtained under continuous illumination which pointed to an important role of hydrogen-containing surface sites in the photoassisted formation of CD_3H from UV-illuminated CD_3I/ZnO systems.[34]

Evidence presented recently by McArthur, Bliss and Butt identified acetaldehyde as another species experiencing strong depletive chemisorption on zinc oxide and exhibiting rapid desorption in some conditions.[35] A steady state acetaldehyde pressure of 10^{-4}N m^{-2} was, therefore, established over a previously outgassed new zinc oxide surface for 60 min to enable some such depletive chemisorption to proceed in the CH_3CHO/ZnO system prior to flash illumination. When the dark-equilibrated CH_3CHO/ZnO interface was then flash-illuminated through a Kodial window, transient increases in ion current with longer rise times and decay times than those shown in Fig. 3 or Fig. 6 were measured (cf. Fig. 9d) at many *m/e* values and are summarized in Fig. 8. The total height of each column at any *m/e* value in that figure represents the maximum increase in ion current achieved (within ca. 200 ms) in the time profile of a flash-initiated transient monitored experimentally at that *m/e* value. Figure 8 thus presents a mass histogram, the 'intensity *vs.* *m/e* pattern' of which is determined by composition of additional gas released into the gas phase above the flash-illuminated surface. Such representations will here be termed 'flash histograms'. An attempt is made in Fig. 8. to illustrate the extent to which *m/e* distribution in the flash histogram could be accounted for by flash-initiated desorption of acetaldehyde. For this purpose the flash histogram was compared with the *m/e* distribution observed experimentally from gaseous acetaldehyde at identical mass spectrometer settings. These two *m/e* distributions have been normalized in Fig. 8 at *m/e* 29. The proportion of each column height at other *m/e* values which is shown blackened-in on Fig. 8 then represents the extent to which observed transients were accounted for by flash-desorbed acetaldehyde. System transients account for apparent lack of agreement at *m/e* 12, 16, 18, 28 and 44. Inspection of Fig. 8 at other *m/e* values shows sufficient agreement to

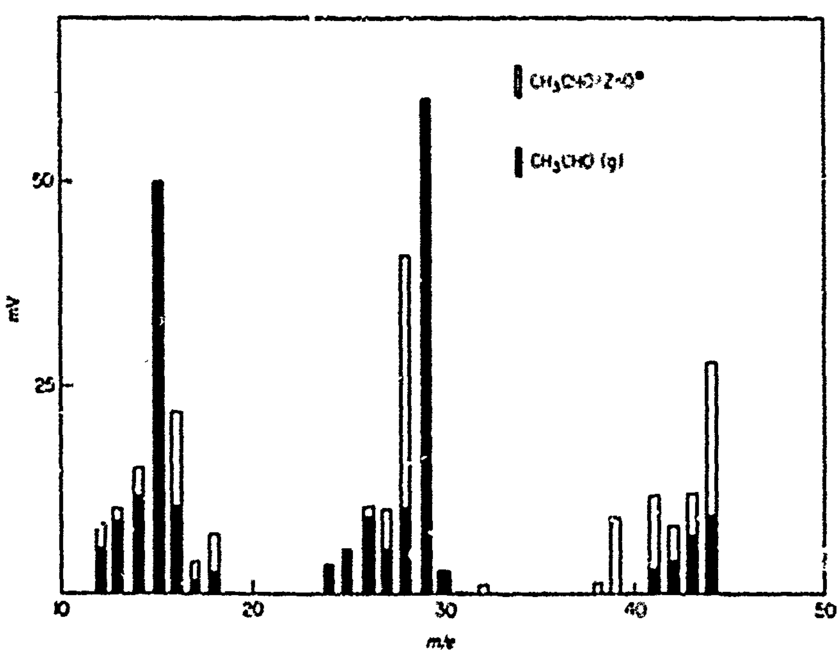

Fig. 8. 'Flash histogram' of species released into the gas phase from a CH_3CHO/ZnO^* interface by flash illumination through a Kodial glass envelope at a pressure of 10^{-4}N m^{-2}. The total column height denotes the maximum increase in ion current measured at the indicated *m/e* value ca. 100–200 ms after the flash. Filled-in heights denote the extent to which the observed changes in ion current can be accounted for by photodesorption of CH_3CHO unchanged from the surface.

support the conclusion that photodesorbed acetaldehyde is the major component of the gases released from the flash-illuminated CH_3CHO/ZnO^* interface. Acetaldehyde thus resembles oxygen both in depletively chemisorbing on zinc oxide and in photodesorbing from it chemically unchanged.

Flash-initiated transients in systems exhibiting cumulative chemisorption

D_2/ZnO. A brief examination was made of the (D_2/ZnO-In) interface as that most likely to carry cumulatively chemisorbed species at room temperature prior to flash illumination. Indium-doped zinc oxide was selected for this study because of reports that doping with tervalent ions enhanced rapid hydrogen chemisorption.[14] Fresh samples of indium-doped zinc oxide on quartz substrates were well-outgassed at 350°C under high vacuum (10^{-6}N m^{-2}) and later exposed to 10^{-4}N m^{-2} pressure of deuterium at room temperture. Flash illumination incident onto the D_2/ZnO-In interface through a quartz window produced no transient changes in signal level at *m/e* 4. The higher resolution settings of the mass spectrometer needed to achieve <5% valley between adjacent peaks at *m/e* 4, 3 and 2, reduced the sensitivity of the system below that achieved in studying transients from O_2/ZnO^* or N_2O/ZnO^*. Nonetheless, this absence of any flash-initiated transient changes at *m/e* 4 was surprising in view of literature reports[16] that hydrogen photoadsorbs onto zinc oxide. Small flash-initiated transients were observed at *m/e* 2 with rise times of 60 ms, but it appeared possible that these originated from molecular hydrogen produced via photolysis of hydrogen-containing surface hydroxyls. Since it appeared probable that surface hydroxyls would be numerically more abundant on a sample of pure zinc oxide (SP-500) because of its greater specific surface area, a sample of ZnO-SP500 was flash illuminated under similar conditions to those used for the indium-doped zinc oxide. In preparing this zinc oxide sample, the powdered catalyst was boiled with deuterated water to promote H/D exchange and obtain some surface hydroxyls of the form OD^-. Subsequent heat treatment and outgassing *in vacuo* were performed in the usual manner prior to flash illumination. Flash-initiated transients at *m/e* 4, 3 and 2 were observed from this sample with rise times of 60 ms. Appearance of transients at *m/e* 4 and 3 in addition to the transient at *m/e* 2, which alone appeared for the ZnO-In sample prepared from a slurry in water, was consistent with production of HD and a little D_2 via photolysis of some surface hydroxyls of form OD^- on the zinc oxide sample boiled in deuterated water. Flash illumination of this latter sample after introduction of deuterium above the solid in the high-vacuum system yielded no flash-initiated transient at *m/e* 4 but did yield a transient of new time profile at *m/e* 3. This had a rise time of 500 ms, as compared with the 60 ms rise time for the HD produced via photolysis. A component with the longer rise time was also apparent in the flash-initiated transient at *m/e* 2 but nothing appeared at *m/e* 4. These preliminary observations on the D_2/ZnO^* system appear consistent withoccurrenceof a relatively slow H/D exchange involving interaction of previously absorbed deuterium with surface hydroxyls sites (OH^-)[4], activated by the flash.

Ethanol/ZnO and TiO_2. Ethanol had been reported as undergoing cumulative chemisorption onto zinc oxide. Ethanol/ZnO^* systems were first examined by the dynamic mass spectrometric technique without any other gas-phase species present in an effort to determine the extent to which the alcohol molecules themselves exhibited photosorption or photoassisted surface reactions. Blank experiments with light from the flash-tube transmitted through a quartz envelope into the vacuum system containing a steady state pressure (7×10^{-4}N m^{-2}) of ethanol showed no flash-initiated enhancement of ions at *m/e* 31, 27 or 26. This absence of any flash-initiated photolysis of ethanol, or of desorption by ethanol-related species from the quartz or metal walls of the vacuum system, made it appear feasible to examine flash-initiated processes for C_2H_5OH/ZnO^* samples using a quartz window. A time profile of flash-initiated changes in ion current at *m/e* 31 from its stable value detected prior to the flash is illustrated in Fig. 9(a). This profile indicates that the molecular species responsible for the flash-initiated transient at *m/e* 31 experienced, firstly, a relatively fast photodesorption process and secondly a slower process which persisted for longer than 8 s and resulted in an over-all lowering of ethanol pressure in the system at times 1 s to 8 s after the flash. Time profiles of transients at *m/e* values for other major ion fragments characteristic of ethanol (e.g. *m/e* 29 and 27) also showed the two major features of Fig. 9(a), i.e. initial fast flash-

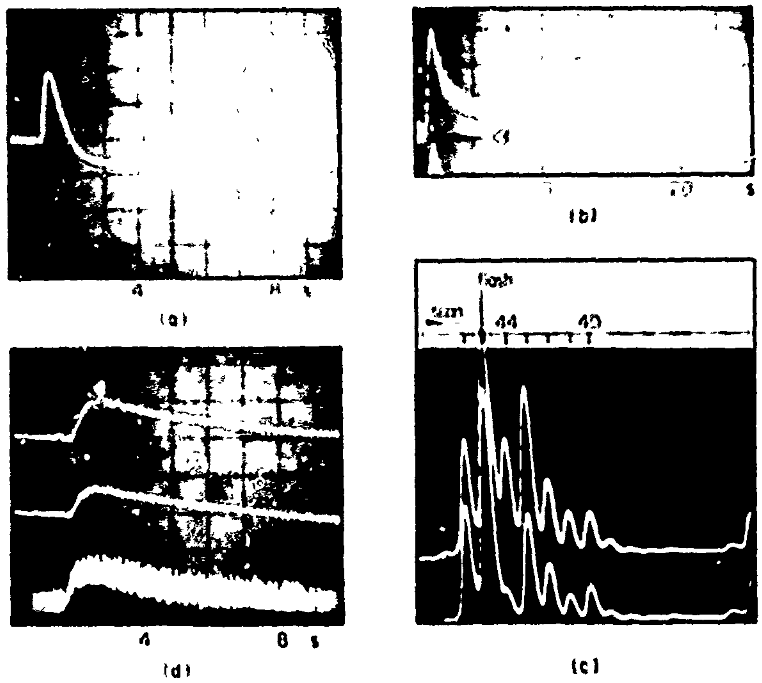

Fig. 9. Oscilloscope trace recordings illustrating transient changes in the ion current initiated by light pulses incident onto ethanol/metal oxide interfaces. (a) Transient (monitored with a sensitivity of 50 mV/div) at *m/e* 31 for flashes incident via a quartz envelope onto a C_2H_5OH/ZnO^* interface. (b) Transient (monitored with sensitivity 20 mV/div) at *m/e* 30 for flash incident via Kodial glass envelope onto a $C_2D_5OD/TiO_2{}^*$ interface. (c) Partial mass scan of ion fragments from gases present in the vacuum system ca. 200 ms after the flash-initiated release of acetaldehyde into the gas phase from a $C_2H_5OH/TiO_2{}^*$ interface. The lower mass spectrum was taken without flash. That marked 'flash' was timed to sweep through *m/e* 43, 200 ms after the flash. (d) Transient at *m/e* 34 monitored at a sensitivity of 20 mV/div for light incident onto a C_2D_5OD/ZnO^* interface via a Kodial glass envelope.

initiated desorption and slow persistent depletion of alcohol from the gas phase over the flash-illuminated zinc oxide surface for times longer than 8 s after the flash. Furthermore, if gas-phase ethanol was pumped away from a C_2H_5OH/ZnO system and the surface then flash illuminated, the observed time profiles showed the fast, flash-initiated photodesorption at *m/e* 31, 29 or 27 attributable to preadsorbed ethanol but *not* the slow persistent depletion. The latter greatly resembled the depletion of gas phase oxygen shown in Fig. 5 for $O_2/TiO_2{}^*$ or of gas-phase nitrous oxide shown in Fig. 7 for "N"N"O/ZnO*, and may likewise be attributed to reaction of ethanol with the previously illuminated metal oxide surface. Conditions favouring the initial fast photodesorption processes and minimizing the slower reaction of ethanol with the flash-illuminated surface were achieved by utilizing a cylindrical illumination window of Kodial glass rather than quartz. In these conditions each measured transient corresponded to a flash-initiated *increase* in ion current rising to its maximum at between 100 and 200 ms after the flash without depletion after the flash, (cf. Fig. 9b). Peak heights of transients measured with experimentally identical conditions (except that *m/e* was set to a different value prior to successive flashes) are assembled into flash histograms in Figs. 10(a) and (c). These display the *m/e* distribution of ion fragments characterizing gases released into the gas phase within ca. 200 ms from C_2D_5OD/ZnO^* and $C_2D_5OD/TiO_2{}^*$ interfaces, respectively. Also shown in Fig. 10 for comparison with these flash histograms is a mass spectrum of ethanol-d_6 recorded with identical instrumental settings but for alcohol vapour which had not contacted the metal oxide. Marked differences between the flash histograms and the mass spectrum in Fig. 10 demonstrate conclusively that, unlike the CH_3CHO/ZnO^* case (cf. Fig. 8), which photodesorbed without significant chemical change in the originally adsorbed molecules, the flash-illuminated C_2D_5OD/ZnO^* and C_2D_5OD/TiO_2^* systems released gases dominated by components other than the originally adsorbed ethanol-d_6.

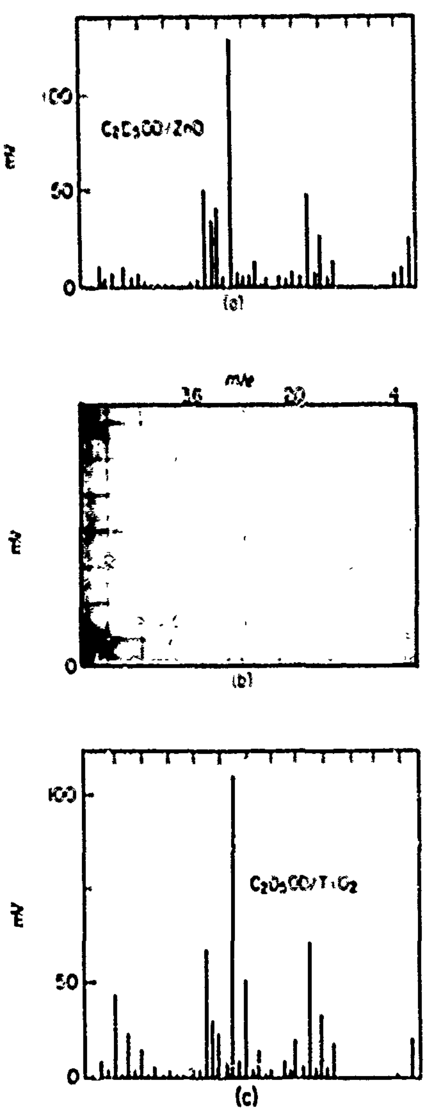

Fig. 10. (a) Flash histogram showing intensity vs. *m/e* pattern for transient changes in ion current initiated by light pulses incident via a Kodial glass envelope onto a ZnO surface under a pressure of 3 × 10^{-4}N m^{-2} of C_2D_5OD. (b) Oscilloscope trace recording of the mass spectrum of $C_2D_5OD(g)$ at pressure 3 × 10^{-4}N m^{-2} measured with similar QMS settings to those used in (a). (c) Similar to (a) but for the C_2D_5OD/TiO_2^* interface at pressure 3 × 10^{-4}N m^{-2}.

Figure 10 thus provided good evidence for extensive photoassisted reaction between ethanol and zinc oxide or titanium dioxide surfaces even when flash-illuminated through a Kodial envelope. Comparison of the mass distribution in mass histograms in Fig. 10 with that shown in Fig. 8 for the acetaldehyde/ZnO* system revealed sufficient similarities to suggest that flash-desorbed acetaldehyde was also a major component of gases released from the ethanol/metal oxide systems (in comparing Fig. 8 with Fig. 10a, allowance must be made for the effects of deuterium substitution on the C_2D_5OD flash histograms). An experimental test of this idea for the ethanol/TiO_2 system was devised as follows. According to the flash histogram for this system (c.f. Fig. 10c) suitable mass spectrometer settings were available which enhanced flash-initiated transients in the *m/e* 40-50 values range much above contributions made by ion fragments of ethanol in that region. Figure 8 shows that flash-desorbed acetaldehyde should contribute significant transients at *m/e* 44, 43, 42 and 41. Consequently, if acetaldehyde was a major component of the flash-initiated gases, a mass scan through the region *m/e* 45–40 at ca. 200 ms after incidence of a flash onto a C_2H_5OH/TiO_2 system should show an enhancement of peak heights at *m/e* 44–41 relative to scanning prior to the flash. Figure 9(c) demonstrates that the expected enhancement at *m/e* 44 and 43 were obtained for a C_2H_5OH/TiO_2* system flash illuminated through Kodial. Photoassisted dehydrogenation of ethanol to acetaldehyde is thus confirmed as an important photoeffect at the flash-illuminated ethanol/TiO_2* interface. With this identification in mind, re-inspection of Figs. 10(a) and (c) reveals the expected large transient at *m/e* 30 due to the major ion fragments (CDO^+) expected from any CD_3CHO produced by photodehydrogenation of C_2D_5OD. Photo-produced CD_3CDO should also give rise to transients at *m/e* 48 and *m/e* 46, which would correspond to CD_3CDO^+ and CD_2CDO^+, but their very small magnitude indicates that not all of the transients at *m/e* 30 can originate from acetaldehyde. Photodesorption of alcohol, which would also contribute transients with *m/e* 30, is another probable process, in view of occurrence of significant transients at *m/e* 34, 33, 32 and 28 with relative proportions similar to those evident in the mass spectrum of C_2D_5OD (compare Fig. 10b with Fig. 10 a or c). Ethanol photodesorption and dehydrogenation are thus indicated at its interface with flash-illuminated zinc oxide or titanium dioxide. Problems in further defining the relative importance of these and other photoassisted processes at these interfaces are considerable, and derive in part from the possibility of selective desorption of one species and in part from the possible role of surface impurities such as hydroxyls in modifying surface photoeffects. It is relevant to summarize our experimental observations on the influence of surface sites and surface species upon total magnitude of such photoeffects.

Information on possible roles of surface hydroxyls was sought in the first instance by comparing the flash histograms obtained using ethanol-d_6 containing 5% D_2O with those shown in Fig. 10 and obtained using anhydrous ethanol-d_6. It was expected that the D_2O component would be chemisorbed, at least in part, as hydroxyls onto the previously well-outgassed zinc oxide or titanium dioxide surface. Flash histograms from the (C_2D_5OD + D_2O)/TiO_2* system showed no significant change from the transients summarized in Fig. 10(c), which was unexpected in view of previous reports that surface hydroxyls assisted photo-oxidation of isopropanol over titanium dioxide exposed to continuous illumination.[18b] The magnitude of transients in the (C_2D_5OD + D_2O)/ZnO* system was, however, reduced to between 20% and 50% of the values observed with anhydrous C_2D_5OD/ZnO*, thus suggesting an inhibiting effect of surface hydroxyls upon photoeffects in this system.

Adsorption—desorption experiments with ethanol/ZnO and ethanol/TiO_2 systems using the vacuum electromicrobalance at ethanol pressures of 10^{-1}—10^{2}N m^{-2} established that adsorption at room temperature obeyed Freundlich isotherms. Extrapolation of these isotherms to the actual pressures, 10^{-5}—10^{-3}N m^{-2}, used in the flash-illumination experiments yielded estimates of equilibrium coverage. These would correspond to only 0.2% of the surface sites of zinc oxide being occupied by ethanol molecules and 2.5% of the surface sites on titanium dioxide being occupied at 10^{-3}N m^{-2} pressure. The magnitude of the transients from the C_2D_5OD/TiO_2* system (Fig. 10c) do not show greater photoeffects equivalent to this greater equilibrium coverage. The possibility was therefore investigated that ethanol molecules strongly chemisorbed onto a few active sites were mainly responsibile for the observed photoeffects. For these investigations, outgassed surfaces of zinc oxide or titanium dioxide were exposed to ethanol at 10^{-2} N m^{-2} for 30—360 min and then the gas-phase ethanol was pumped away for periods of from 1 to 18 h. Surfaces thus pre-exposed to ethanol were then flash illuminated and the observed transient assembled into flash histograms. These showed qualitative similarities to the flash histograms measured when ethanol vapour was present, e.g. parent and fragment ions of acetaldehyde were clearly evident, but over-all the transients were reduced in magnitude by 80—90%. The histograms also showed components corresponding to flashdesorption of ethanol, thus making clear the existence of strongly adsorbed molecules on the interfaces even after prolonged pumping.

4. Conclusion

The results described were mainly concerned with photoeffects produced by flashes of UV light incident upon zinc oxide or titanium dioxide surfaces in the presence of a single reactant gas (not oxygen). Therefore, true photocatalysed reactions between two or more gases over the illuminated interfaces were not observed. Nevertheless, a wide range of effects was observed, including: photolysis of hydrogen-containing surface groups; photoassisted H/D exchange in D_2/ZnO* systems; photodesorption of acetaldehyde and ethanol; photoassisted reduction of nitrous oxide or methyl iodide and photoassisted oxidation of ethanol via chemical reaction with the flash-activated surfaces. The results demonstrate the great utility of the present dynamic mass spectrometric technique for distinguishing such processes in cases where two of these photoeffects proceeded simultaneously but with different reaction velocities at the flash-illuminated surfaces (e.g. fast photodesorption of nitric oxide product from N_2O/ZnO* interfaces was readily time-resolved from depletion of nitrous oxide by slow chemical reaction with ZnO*; and fast release of HD via photolysis of surface OH and OD groups on zinc oxide was readily distinguished from slower production of HD via interaction of adsorbed deuterium with light-activated surface hydroxyls). This aspect of the technique is capable of further development in future studies.

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Photoeffects involving Oxygen-18 at Flash-illuminated ZnO and TiO_2 Surfaces

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The extent of surface coverage of TiO_2 and various zinc oxides by chemisorbed oxygen is compared with relative efficiencies for photodesorption of $^{18}O_2$, as initiated by 50 μs light pulses and measured by a dynamic mass spectrometer technique. The results can be understood within the framework of the Electronic theory.

In an earlier publication, we considered the possible relevance of Localised Surface Site and Electronic Band Theory models to real surfaces of semiconducting ZnO and TiO_2 and to photoeffects produced at such surfaces by 50 μs pulses of u.v. photons. Experimental details and preliminary results were presented for a dynamic mass spectrometer technique capable of monitoring time-profiles for release of species into the gas phase above the flash-illuminated metal oxide surfaces. More recent results of this technique, obtained by use of oxygen enriched in ^{18}O, are presented in this Note and are briefly considered in the narrow context of agreement or disagreement with the previously-presented Electronic Band Theory model of ZnO and TiO_2 surfaces.[1, 2]

Electronic band theory descriptions of oxygen chemisorption [3-5] onto the n-type semiconducting solids ZnO and TiO_2 envisage conversion of some fraction of physically absorbed oxygen, to O_2^-(ads), and possibly O^-(ads), through localisation of electrons from the conduction band or from surface donors in thermal equilibrium with this band, *i.e.* (1*a*) followed by (1*b*) or (1*c*).

$$O_2(g) \rightleftarrows O_2(ads) \tag{1a}$$

$$O_2(ads) \overset{e^-}{\rightleftarrows} O_2^-(ads) \tag{1b}$$

$$O_2(ads) \overset{e^-}{\rightleftarrows} O^-(ads) + O(ads). \tag{1c}$$

In this study a Sartorius vacuum microbalance was used to obtain estimates of the extent of surface coverage by physically adsorbed or chemisorbed oxygen, these being distinguished experimentally on the basis that only the former was reversibly removed upon pumping off gas-phase oxygen at room temperature. Results are entered in table 1 for TiO_2 and for three types of zinc oxide selected because of widely different concentrations, η_e, of conduction band electrons.[5] Nett weight increases registered by samples when equilibrated with various oxygen pressures in the range 10-250 N m^{-2} were too small for accurate measurement with Li-ZnO. For pure ZnO and In-ZnO, total weight increases varied with pressure approximately in accordance with the Freundlich isotherm. The reversible nature of most oxygen adsorption on these solids at room temperature was demonstrated by removal >90 % of the adsorbed oxygen upon evacuation. This is termed O_2(rev). Restoration of sample weight to determined with potassium ferrioxalate actinometer. These very low efficiencies would be consistent with either the interaction of the small surface coverage by O_2(chem) with holes via (*3a*) or with excitons via (*3b*).

$$O_x^-(\text{ads}) + h^+ \rightarrow O_x(\text{ads}) \tag{3a}$$

$$O_x^-(\text{ads}) + (e-h) \rightarrow O_x(\text{ads}) + e^- . \tag{3b}$$

The symbol O_x^-(ads), where $x = 2$ or 1, is used to retain the generality of the nature of chemisorbed oxygen. Regardless of its exact nature, our values of O_2(chem) in table 1 indicated that the extent of surface coverage by O_x^-(ads) varied in the sequence TiO_2 > In—ZnO > ZnO > Li—ZnO. The same sequence is followed for the relative efficiencies of $^{18}O_2$ photodesorption (*cf.* the last row of table 1) and this would be expected if surface coverage by O_x^-(ads) determined the efficiency of process (*3a*) or (*3b*) in competition with electron-hole recombination.

The time profile in fig. 1 for release of $^{18}O_2$ to the gas phase following flash-excitation of the $^{18}O_2$/metal oxide interface illustrates that flash desorption of $^{18}O_2$ was not immediate. This follows from the fact that observed rise-time to Δ_{max} was *ca.* 0.2s at $m/e = 36$ for these $^{18}O_2$/metal oxide[6] interfaces, whereas response-time of the system, as demonstrated by studies on other systems, was very much faster with minimum rise-times, ~0.02s. The observed slow release of $^{18}O_2$ to the gas phase could not arise directly from (*3b*), in view of short exciton lifetimes. Slow release could, however, arise if O_2(ads) produced by (*3b*) or (*3a*) desorbed only slowly via a thermally-assisted process. Alternatively if the charge-neutralization represented by (*3a*) were controlled by slow diffusion of holes to the interface after a flash, this could also slowly yield molecular oxygen. These alternatives have not been resolved by this study.

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Oxygen Intermediates at Flash-illuminated Metal Oxide Surfaces studied by Dynamic Mass Spectrometry

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ABSTRACT Information is presented on short-lived oxygen intermediates at surfaces of metal oxide catalysts. Application of a dynamic mass spectrometer technique yielded time-profiles of mass-resolved changes in pressure or composition of gases over the catalyst surfaces following illumination with a u.v.-pulse of 50 μs duration. Flash-illumination of Cr_2O_3, Fe_2O_3, or ZnO in the presence of 2×10^{-4} N m^{-2} of $^{18}O_2$ resulted in appearance of isotopically scrambled oxygen with post-flash rise times of 0·1 s. Evidence is presented that scrambling stems from oxygen-16 intermediates produced by flash photolysis of the metal oxide. Relative efficiencies for four flash-initiated processes involving oxygen are presented for $^{18}O_2$ in contact with oxides of first-row transition metals. Results of experiments carried out with low pressures of N_2O and/or aliphatic alcohols present at flash-illuminated zinc oxide surfaces are shown to be consistent with formation and reaction of $^{16}O^-$ at the gas/solid interface.

INTRODUCTION

Surfaces of zinc oxide or titanium dioxide have been reported to exhibit additional catalytic activity, relative to the non-illuminated system, when simultaneously exposed to u.v.-illumination, molecular oxygen, and an oxidizable reactant.[1-4] Prominent examples of such photocatalytic activity include oxidation of hydrogen or carbon monoxide,[5,6] partial oxidation of C_3—C_{10} alkanes to corresponding aldehydes or ketones[7,3] over TiO_2 and the photosynthesis of H_2O_2 in u.v.-illuminated oxygenated aqueous suspensions of ZnO. A mechanism recently suggested for this latter process by Dixon and Healy[8] typifies one general hypothesis concerning these photocatalysed oxidations, since it involves both the formation of an active oxygen intermediate on the metal oxide surface (O_2^- in that case) and product formation by reaction between oxidizable reactant and the oxygen intermediate on the surface. The present study attempts, by application of fast detection techniques, to develop information on the reactivity, lifetime, and identity of any such oxygen intermediates produced at metal oxide surfaces by intense pulses of u.v. photons.

EXPERIMENTAL

Metal oxides were used as finely divided powders of highest purity available commercially, *viz.* oxides of first-row transition metals as spectroscopically pure standards from Spex Industries, and research-grade TiO_2 (Code TiO_2-MR 128) or ZnO (Code ZnO-SP 500) obtained through the courtesy of New Jersey Zinc Co. Surface areas were determined from N_2 adsorption at 77 K using a Sartorius vacuum microbalance. Thin layers of metal oxide on a quartz substrate were prepared by coating it with a thick paste made from 0·2–1·0 g of metal oxide in triply distilled water and subsequent vacuum-evacuation, first at 350 K and finally at 623 K for 16 h at 10^{-4} N m^{-2}.

Nitrous oxide enriched to >95% in nitrogen-15 at the central atom was used as obtained from Stohler Isotopes. Oxygen enriched to >98% in oxygen-18 was obtained from Miles Laboratories. Reagent grade alcohols were dried, distilled from molecular sieve, and purified by trap-to-trap distillations prior to use.

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Procedures. The great majority of experiments here reported were carried out in *dynamic* conditions with gas at reduced pressure of 2×10^{-4} N m^{-2} flowing continuously over a metal oxide catalyst to an ion-pump of 80 l s^{-1} pumping speed. Full details have been published elsewhere[9,10] of the high-vacuum system, of the equipment utilized to deliver 50 μs light pulses to these dynamic gas/metal oxide interfaces and of the dynamic mass spectrometer (DMS), used to monitor time-profiles of flash-initiated changes in gas phase pressure or composition.

Use of an asterisk thus, gas/metal oxide*, denotes a u.v.-illuminated interface and more conventional studies of photoeffects were made in *static* conditions at such interfaces by contacting reactant gas(es) at pressures 10—1000 N m^{-2} with vacuum-activated metal oxide surfaces at room temperature and then continuously illuminating them by photons of λ = 254 nm. Pressure measurements with an Edwards type GC 52 Pirani gauge and analysis of samples by a CEC 021-620A mass-spectrometer were employed to identify products and their increase with time.

Relative efficiencies of photoassisted processes

A potassium ferrioxalate actinometer located in the elliptical cavity of the 50 μs flash-tube was used to obtain values of "photons incident per flash". Relative efficiencies, ϕ, of flash-initiated changes in pressure of $^{18}O_2$, $^{16}O_2$, or ^{16}O–^{18}O were derived by dividing measured increases (or decreases) of gas phase oxygen by the appropriate value of photons per flash.

Results and Discussion

No evidence for isotopic exchange between flowing $^{18}O_2$ and oxygen-16 of metal oxide surface was obtained at room temperature in the dark at 2×10^{-4} N m^{-2} since the isotopic composition of the $^{18}O_2$ gas remained unaffected. Exposing dark-equilibrated $^{18}O_2$/metal oxide interfaces to the output of the flash-tube, produced readily measurable changes in signal level at m/e = 36, 34, or 32. Time-profiles of representative changes at m/e = 36 and 34 are illustrated in Figure 1 for the flash-illuminated $^{18}O_2$/Cr_2O_3* interface. The two upper traces of Figure 1 were measured with light incident

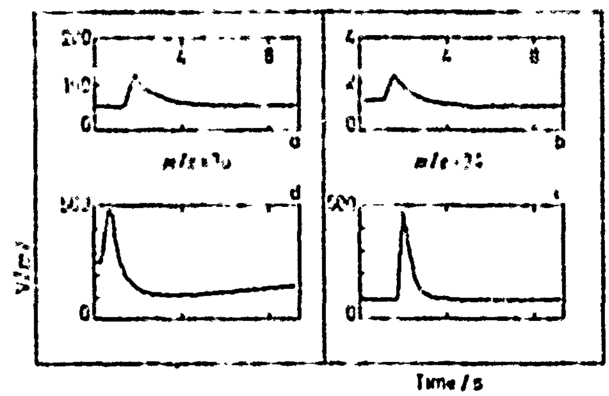

FIGURE 1 Oscilloscope traces showing time profiles of flash-initiated changes in signal level (V/mV) monitored at m/e = 36 or 34 during and after flash-illumination of the $^{18}O_2$/Cr_2O_3 interface. *Top*: Changes initiated by flashes incident through a 38 A filter monitored at m/e = 36 (trace a) and m/e = 34 (trace b) at indicated sensitivities. *Bottom*: Change initiated by flashes incident *via* quartz monitored at m/e = 36 (trace d) and m/e = 34 (trace c).

via a 38A filter and show very similar time profiles for appearance of additional $^{18}O_2$ or ^{16}O-^{18}O in the gas phase. The relative magnitudes of the maximum post-flash increases (Δ^+_{max}) are 50 mV and 2 mV, respectively, for $m/e = 36$ and $m/e = 34$, which is the same as the relative abundance of $^{18}O_2$ and ^{16}O-^{18}O in the gas phase. Furthermore, both rise to 50% of Δ^+_{max} in half times, $t_{½}^+$, of 0·1 s. Photoeffects for $^{18}O_2/Cr_2O_3{}^*$ *via* a 38A filter are thus consistent with flash-assisted desorption of molecular oxygen having the same isotopic composition as the gas phase and show no isotopic scrambling. Similar observations were made and the same conclusion drawn for all the metal oxides flash-illuminated *via* a 38A filter in this study.

The lower traces of Figure 1 were measured with the full output of the flash tube incident on to $^{18}O_2/Cr_2O_3$ *via* a quartz envelope. Time profiles measured at $m/e = 36$ in these conditions reveal, not only a rapid flash-initiated desorption of $^{18}O_2$ similar to that in the upper trace of Figure 1, but also a slower process which caused $P(^{18}O_2)$ to decrease at times 0·2 to 1·5 s after a flash and to remain below the pre-flash steady-state value for post-flash times up to 28 s. This latter process is not of central concern in this paper but can reasonably be interpreted[10] as an uptake of molecular oxygen occurring *via* collisonal encounter of $^{18}O_2(g)$ with relatively long-lived ($t_{½} \geq 15$ s) reactive centres produced by the flash at the $O_2/Cr_2O_3{}^*$ interface. As such it serves to illustrate the slow time-profiles expected for processes requiring post-flash collision of gas phase molecules with the flash-activated surface.

If the signal level at $m/e = 34$ were influenced only by the two flash-initiated processes which affected $m/e = 36$, then the time-profile at $m/e = 34$ should correlate closely with that measured at $m/e = 36$ in similar conditions, but with features reduced to 4%. Comparison of traces c and d of Figure 1 reveals instead that the time profiles are very different and that $m/e = 34$ consists mainly of a rapid rise with $t_{½}^+ \sim 0{\cdot}1$ to $(\Delta^+_{max}) \sim 320$ mV. This is disproportionately large relative either to Δ^+_{max} for $m/e = 36$ in another flash or to the decrease (Δ^-_{max}) (*cf.* trace d of Figure 1). The discrepancy in size, together with the "fast" profile of this transient, are taken as evidence for a flash-initiated oxygen-scrambling process involving preadsorbed $^{18}O_2$ and an oxygen-16 species on the surface of flash-activated Cr_2O_3. No evidence for release of ^{16}O to the gas phase was obtained, but measurements were made on flash-initiated changes at $m/e = 32$ as an indication of extent of formation and combination of oxygen-16 species on the surface of flash-activated Cr_2O_3. Such measurements demonstrated much-enhanced "fast" release of $^{16}O_2$ from $^{18}O_2/Cr_2O_3$ under flash-illumination through quartz ($\Delta_{max} = 230$ mV at $m/e = 32$) than through the 38A filter ($\Delta_{max} \sim 0{\cdot}3$ mV). When taken together with our observation that significant oxygen-scrambling occurred for flash-illumination incident through quartz but not through the 38A filter (*cf.* traces b and c of Figure 1), the data point strongly to probable involvement of oxygen-16 fragments produced by flash photolysis of the Cr_2O_3 surface in the flash-initiated oxygen-scrambling.

The main characteristics of the four flash-initiated processes distinguished at the $^{18}O_2/Cr_2O_3{}^*$ interface by the DMS technique may be summarized as follows:

Process I: Increase with $t_{½}^+ \sim 0{\cdot}1$ s of signal $m/e = 36$, attributable to flash-initiated desorption of preadsorbed $^{18}O_2$.

Process II: Slow decrease with $t_{½}^- \sim 1$ s of signal at $m/e = 36$ attributable to uptake of $^{18}O_2$ from the gas phase by interaction with active long-lived centres produced on the metal oxide by a flash.

Process III: Increase with $t_{½}^+ \sim 0{\cdot}1$ s of signal at $m/e = 32$, attributable to formation of $^{16}O_2$ by photolysis of the metal oxide.

Process IV: Increase with $t_{½}^+ \sim 0{\cdot}1$ s of signal at $m/e = 34$ attributable to desorption of ^{16}O-^{18}O produced by interaction of preadsorbed $^{18}O_2$ with oxygen-16 species from lattice photolysis.

In order to test whether these processes were of general occurrence, thin layers of the stable oxides of other first-row transition metals were prepared, vacuum-activated and flash-illuminated in identical manner to $^{18}O_2/Cr_2O_3$*. Results of this survey are presented in Table I as relative efficiencies (*cf.* Experimental Section). Absence of any entry for a process indicates that flash-initiated changes in signal-level were too small for certain detection with the prevailing noise level. This effectively limited observable processes to those having relative efficiencies $\geq 3 \times 10^{-7}$. Inspection of Table I shows that, with 2×10^{-4} N m^{-2} pressures of $^{18}O_2$ present over the various metal oxides, one or more of processes I—IV was readily measurable for all oxides except NiO. Entries in Table I have been corrected for any small changes measured in blank experiments carried out with light incident on to the $^{18}O_2$/quartz substrate interface. Entries in parentheses show, for comparison, the relative efficiency, if any, of the same flash-initiated process when light was incident on to the metal oxide *in vacuo* prior to its exposure to $^{18}O_2$. The following trends emerge:

Process I: Presence of $^{18}O_2$ caused a significant increase in photodesorption of $^{18}O_2$ for all except the *p*-type semiconducting metal oxides NiO, CuO, and CoO. This trend appears fully consistent with arguments presented elsewhere by the authors[9,10] that availability of conduction-band electrons (*n*-type semiconductivity), influences extent of O_2 photodesorption, because it controls extent of $O_2^-(s)$ formation at the O_2/metal oxide interfaces prior to the flash.

Process II: This slow long-persisting uptake of $^{18}O_2$ likewise did not occur for the *p*-type metal oxides but was readily measurable for other metal oxides, except V_2O_5, with efficiency increasing in the sequence ZnO < TiO_2 < $Cr_2O_3 \approx Fe_3O_4$. This trend would be consistent with post-flash reaction of gas-phase O_2 with long-persisting surface centres bearing excess negative charge. Such centres could exist at surfaces of *n*-type semiconducting oxides, after a flash, either as lower valency states of the cations or as surface-trapped electrons. Present results do not suffice to distinguish between these possibilities.

Process III: Presence of $^{18}O_2$ at 2×10^{-4} N m^{-2} either decreased the extent of lattice breakdown to $^{16}O_2$ (as occurred for CoO, ZnO, and to lesser extent for V_2O_5 and Fe_3O_4), or increased it (as occurred strongly for Cr_2O_3 and to lesser extent for CuO). Comparison of the efficiencies of Process I with Process III for these various metal oxides reveals no apparent correlation between these processes, such as has been noted elsewhere[9b] for various zinc oxides.

Process IV: Oxygen scrambling with apparent efficiency $>10^{-6}$ was detected only for $^{18}O_2/Cr_2O_3$*, $^{18}O_2/Fe_3O_4$*, $^{18}O_2$/ZnO*, and $^{18}O_2$/CoO* interfaces and these correspond to interfaces which simultaneously underwent photolysis to $^{16}O_2$ with larger or comparable efficiencies. Other $^{18}O_2$/metal oxide* interfaces, which were shown not to photolyse to $^{16}O_2$ with appreciable efficiency also did not produce significant flash-initiated oxygen scrambling. Such correlation between extent of flash-initiated oxygen scrambling and lattice photolysis could be understood if photolysis produced either $^{16}O_x^-$ or $^{16}O_x^{n-}$ intermediates at the surface and these participated in oxygen scrambling *via* (1), with $n = 0$ or 1 and $x = 1$ or 2.

$$^{16}O_x^{n-} + {}^{18}O_2 \rightarrow ({}^{16}O_x{}^{18}O_2)^{n-} \rightarrow {}^{16}O{-}^{18}O + ({}^{16}O_{x-1}{}^{18}O)^{n-} \quad (1)$$

This hypothesis is similar to recent suggestions that $^{16}O^-$ species form on surfaces of ZnO under continuous u.v. illumination[11,12] and contribute to oxygen scrambling or to photocatalysed oxidation of carbon monoxide.[13]

Use of N_2O to enhance O^- formation on illuminated zinc oxide. A technique employed by previous workers[14] to enhance selectively formation of O^- on metal oxide surfaces, and so facilitate study of its reactivity and e.s.r. spectrum[11,15] involves transfer of an

Table I

Relative Efficiencies of Oxygen Photoeffects Flash-Initiated *via* Quartz

System	Efficiency of Process[a]			
	I $m/e = 36$	II $m/e = 36$	III $m/e = 32$	IV $m/e = 34$
$^{18}O_2/TiO_2$*	$4{\cdot}4 \times 10^{-6}$	$-5{\cdot}6 \times 10^{-5}$	$4{\cdot}0 \times 10^{-7}$	—
vac/TiO_2*	$(2{\cdot}0 \times 10^{-7})$	—	—	—
$^{18}O_2/V_2O_5$*	$3{\cdot}5 \times 10^{-6}$	—	$1{\cdot}2 \times 10^{-5}$	—
vac/V_2O_5*	$(5{\cdot}0 \times 10^{-7})$	—	$(2{\cdot}0 \times 10^{-5})$	—
$^{18}O_2/Cr_2O_3$*	$2{\cdot}5 \times 10^{-5}$	$-1{\cdot}0 \times 10^{-4}$	$2{\cdot}3 \times 10^{-5}$	$3{\cdot}0 \times 10^{-5}$
vac/Cr_2O_3*	—	—	$(4{\cdot}0 \times 10^{-7})$	—
$^{18}O_2/Fe_2O_3$*	$6{\cdot}3 \times 10^{-6}$	$-1{\cdot}3 \times 10^{-4}$	$6{\cdot}6 \times 10^{-5}$	$4{\cdot}8 \times 10^{-6}$
vac/Fe_2O_3*	—	—	$(9{\cdot}3 \times 10^{-5})$	—
$^{18}O_2/CoO$*	—	$-3{\cdot}4 \times 10^{-6}$	$7{\cdot}4 \times 10^{-5}$	$1{\cdot}2 \times 10^{-6}$
vac/CoO*	—	—	$(2{\cdot}7 \times 10^{-4})$	—
$^{18}O_2/NiO$*	—	$-3{\cdot}4 \times 10^{-6}$	$4{\cdot}2 \times 10^{-7}$	—
vac/NiO*	—	—	$(3{\cdot}0 \times 10^{-7})$	—
$^{18}O_2/CuO$*	—	—	$2{\cdot}9 \times 10^{-5}$	$3{\cdot}5 \times 10^{-7}$
vac/CuO*	—	—	$(1{\cdot}0 \times 10^{-4})$	—
$^{18}O_2/ZnO$*	$1{\cdot}5 \times 10^{-6}$	$-1{\cdot}7 \times 10^{-5}$	$7{\cdot}0 \times 10^{-6}$	$1{\cdot}0 \times 10^{-6}$
vac/ZnO*	—	—	$(4{\cdot}1 \times 10^{-5})$	—

[a] See text for detailed designation of each process.

electron to N_2O from the metal oxide and dissociation according to the overall scheme, (2). Results in this section relate to our attempts to use this process to generate high

$$N_2O_{(g)} \rightleftharpoons N_2O_{(s)} \xrightarrow{e^-/MO} N_2O^-_{(s)} \rightarrow N_{2(g)} + O^-_{(s)} \qquad (2)$$

transient concentrations of O^- at the interface between gaseous N_2O and a flash-illuminated metal oxide and thence to study reactivity of O^-. The feasibility of thus employing gaseous N_2O as a source of additional O^- at a flash-illuminated interface was first checked by observing the effect of $N_2{}^{16}O$ upon the oxygen scrambling process noted above for $^{18}O_2/ZnO$* interfaces. Introduction of $N_2{}^{16}O$ at pressure 3×10^{-4} N m^{-2} caused a four-fold increase in the amount of ^{16}O–^{18}O released from the ($N_2{}^{16}O$ + $^{18}O_2$)/ZnO* interface relative to that measured from the $^{18}O_2$/ZnO* interface. Such an increase was fully consistent with flash-initiated production of additional $^{16}O^-(s)$ species from N_2O *via* (2) and their contribution to rapid oxygen scrambling *via* scheme (1).

Aliphatic alcohols were used as additional tests of O^- involvement, in view of reports that $O^-(g)$ species underwent secondary reaction with alcohols in the presence of nitrous oxide.[18] Warman attributed the appearance of additional product nitrogen to schemes (3a) and (3b).

$$ROH + O^- \rightarrow X \qquad RO^- + OH) \text{ (or } RO + OH^-) \qquad (3a)$$

and

$$X + Y^- + 2N_2O \rightarrow 2N_2 + \text{Products} \qquad (3b)$$

Warman argued that absence of additional N_2 product from tertiary alcohols originated because process (3a), involving abstraction of H or H^{+} from the alcohol, could not occur in the absence of an α-hydrogen.

Results obtained in this study, on the extent of N_2 product formation at N_2O/metal oxide interface in the presence of various alcohols are summarized in Figure 2 and are in

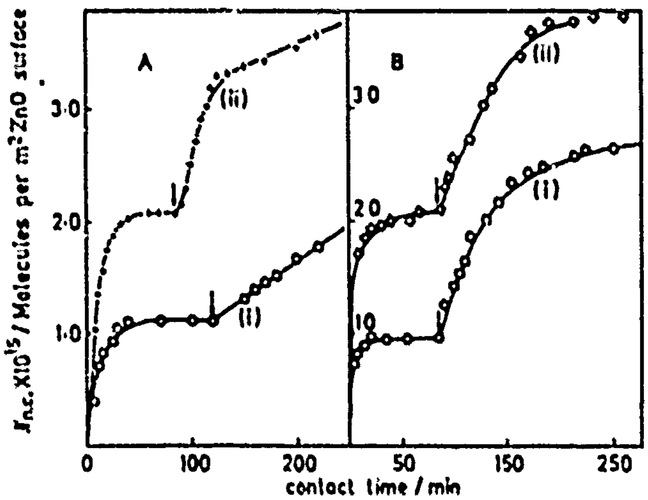

FIGURE 2 Growth of nitrogen product with contact time (minutes) from interactions of zinc oxide with N_2O alone or premixed with aliphatic alcohols. U.v.-illumination of the dark-equilibrated interface by photons (254 nm) was commenced after contact times indicated by an arrow. 2A Trace (i) Gas phase consisting initially only of N_2O. Trace (ii) Gas phase consisting initially of (N_2O + C_2H_5OH). 2B Trace (i) Gas phase consisting initially of (N_2O + Bu^{t}OH). Trace (ii) Gas phase consisting initially of (N_2O + Pr^{i}OH).

good agreement with Warman's explanation. Curve (i) of Figure 2A shows an initial rapid production of N_2 product at the N_2O/ZnO interface in the dark which is in accordance with scheme (2) and published work. Comparison of the N_2 product formed when ethanol (curve ii of Figure 2A) or isopropyl alcohol (curve ii of Figure 2B) were simultaneously admitted to the ZnO interface together with N_2O reveals additional formation of N_2 product—as expected from reaction of O^- with these alcohols in the dark *via* schemes (3a) and (3b). That $O^-(s)$ produced *via* scheme (2) on the ZnO interface retained selectivity similar to gas-phase O^- and did not react with t-butyl alcohol *via* schemes (3a) plus (3b) to produce additional nitrogen, is illustrated by the similarity of the plots for (N_2O + t-butyl alcohol)/ZnO [plot (i) of Figure 2B] and N_2O/ZnO [plot (i) of Figure 2A].

Additional type (2) processes at N_2O/ZnO interfaces had previously been reported under continuous u.v.-illumination and attributed to migration of photogenerated holes to the negatively charged N_2O/ZnO interface.[14b] Additional N_2 product from extra type (3a) and (3b) events were therefore expected, on Warman's mechanism, from illuminated mixtures of N_2O with primary or secondary alcohol. The section of curve ii of Figure 2A which lies immediately to the right of the arrow denoting start of u.v. illuminations, demonstrates an initial rapid rise consistent with u.v. illumination initiating additional production of N_2, probably *via* (2) → (3a) → (3b) at the $(N_2O + C_2H_5OH)/ZnO^*$ interfaces. This system was examined under flash-illumination on the DMS system in the hope that individual steps of this 3-step illumination-induced production of N_2 might thereby be resolved. Time profiles in Figure 3A and 3B allow detailed comparison to be made of fast changes in gas phase pressure of

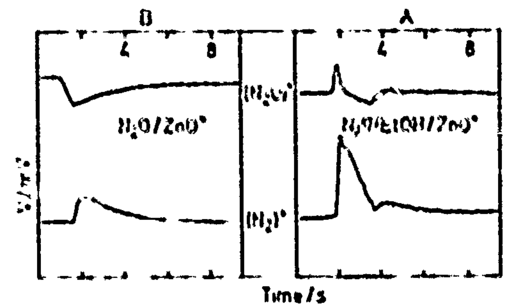

FIGURE 3 Comparison of time-profiles for changes in signal level (V/mV) for N_2O^+ and N_2^+ flash-initiated at an N_2O/ZnO^* or an $(N_2O + EtOH)/ZnO^*$ interface. 3A Upper trace: Profile at $m/e = 45$ ($\equiv {}^{14}N^{15}N^{16}O^+$) from mixture of ${}^{14}N^{15}N^{16}O$ with C_2D_5OD flowing over a flash-illuminated ZnO surface; 3A Lower trace: Profile for flash-initiated production of N_2^+ from $(N_2O + EtOH)/ZnO^*$. 3B Upper trace: Profile of flash-initiated depletion of ${}^{14}N^{15}N^{16}O$ from the gas phase over N_2O/ZnO^*. 3B Lower trace: Profile of flash-initiated growth of N_2 in gas phase above N_2O/ZnO^*.

N_2O and N_2 over the $(N_2O + EtOH)/ZnO^*$ and N_2O/ZnO^* interfaces following identical flash-illumination through quartz. The profile for N_2O^+ over N_2O/ZnO^* shows a decrease in gas-phase N_2O attributable to process (2) at the flash-activated surface and subsequent restoration of the pre-flash steady-state condition within 3s (upper trace Fig. 3B). On the other hand, the trace for N_2O^+ over $(N_2O + EtOH)/ZnO^*$ (upper trace Fig. 3A) indicates an initial rapid desorption of N_2O and superimposed upon that a secondary process which depleted N_2O from the gas phase and resulted in an almost linear section of the profile at times 1—2·5 s after the flash. Our preliminary interpretation of this section is that it arises from step (3b) involving reaction of N_2O from the gas phase with intermediates $(X + Y)^-$ rapidly produced *via* (3a) and involving interaction of O^- with preadsorbed ethanol. As required by this interpretation, the time-profile for production of N_2^+ over flash-illuminated $(N_2O + EtOH)/ZnO^*$ (lower trace in Figure 3A) likewise shows a linear section corresponding to a secondary process yielding additional $N_2(g)$ after fast initial N_2 production (*cf.* lower trace of Figure 3B and note that no linear secondary process was apparent in the time profile for N_2^+ from N_2O/ZnO^*).

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Active Sites for Dehydration and Dehydrogenation of Aliphatic Alcohols over ZnO and TiO_2 at 15-30°C.

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Abstract

The nature of active sites on ZnO and TiO_2 capable of dehydrating or dehydrogenating C_2-C_4 aliphatic alcohols to very limited extent at 15-30°C is examined both for liquid alcohol and alcohol vapour. Absence of ether products in each condition is interpreted as evidence against formation of carbonium ions as important intermediates. Observations that ease of dehydration is greatest for t-butanol are interpreted instead in terms of alcohol interaction with Lewis-acid type surface sites, leading to synchronous loss of OH and H from adjacent carbon atoms. Sites active in this manner are tentatively identified as coordinatively unsaturated metal ions whereas coordinatively unsaturated oxygen ions promote dehydrogenation. Observed effects of uv illumination and of N_2O additions are consistent with this description of active surface sites.

Paper accepted for presentation at *Fifth Iberoamerican Symposium on Catalysis*, Lisbon, July, 1976.

Introduction

Metal or oxygen ions with high degree of coordinative unsaturation, viz., M^{+n}_{cus} or O^{-n}_{cus}, had previously been identified on vacuum-outgassed ZnO or TiO_2 surfaces.[1-4] In this study dehydration and dehydrogenation of alcohols on such surfaces at 15-30°C are examined with two objectives: firstly, to assess the importance of Lewis acid-base character of such active sites in these reactions, and secondly, to examine the role of O^{-}_{cus}. In furtherance of these objectives, and particularly in order to facilitate comparison with published rate constants for reaction of O^{-} with alcohols in homogeneous liquid[5] or gaseous systems,[6] interactions of the metal oxides have here been studied with alcohols both in their liquid and vapour phases.

Experimental

Reagents: Alcohols were Analytical Reagent, or equivalent grade, which were dried over molecular sieve or NaOH and distilled prior to use. Metal oxides were high purity powdered ZnO or TiO_2 supplied by courtesy of New Jersey Zinc Co. as ZnO-SP500 or Rutile MR-128. Samples had similar particle-size distribution, reflectance spectra and surface areas (4.0 and 5.4 $m^2 g^{-1}$ respectively). Oxygen, nitrous oxide and nitrogen were "British Oxygen Grade X" spectroscopically pure gases for mass spectrometric experiments, but were from 'medical' or "white spot" cylinders (BOC) for gas chromatographic experiments.

Procedures: Metal oxide/Alcohol vapour interactions were followed by mass spectrometric analysis (CEC Model 21-601D or Micromass 6 mass analysers) and pressure measurements on conventional vacuum systems routinely attaining residual pressures < 10^{-4} N m^{-2}. For these investigations, ZnO or TiO_2 were deposited as thin layers onto quartz substrates, dried and then outgassed on the vacuum system in conditions reported to reduce surface hydroxyls to low

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levels,[7] viz., 16 hrs at 350° under continuous evacuation at ca. 10^{-4} N m^{-2}. Samples were cooled to room temperature under 10^{-4} N m^{-2} and then a steady flow of alcohol vapour at pressures 10^{-4}-10^{2} N m^{-2} was usually established over the metal oxide, although some preliminary measurements were made with a static system. In some experiments the metal oxide substrate was illuminated through a 'Pyrex' envelope by the output of a 150 watt medium-pressure mercury-arc lamp. Product formation in dynamic conditions were detected either, by mass spectral analysis of gases ca. 10^{-3} sec. after their emergence from the reactor, or by continuously condensing product into a liquid-N_2 cooled trap over 0.5-4 hr contact time and subsequently mass analysing the condensate. Procedures similar to the latter were used to analyse products from the static reactor.

Metal oxide/Liquid Alcohol interactions were investigated by establishing a flow of carrier gas (N_2, O_2 or N_2O) through a suspension of powdered ZnO or TiO_2 in liquid alcohol and then analysing samples of the emergent carrier gas with a Pye 104 gas chromatograph fitted with a flame-ionization detector. Blank runs with no added metal oxide, but with carrier-gas passing through prepared liquid solutions of acetone and isobutyraldehyde in isobutanol, established the validity of utilising carrier gas to sweep out representative vapour phase samples and showed sensitivity to < 0.1% of aldehydic or ketonic product. Liquid samples were also taken at intervals, centrifuged to remove suspended metal oxide particles and injected onto the chromatograph for analysis. Calibration of retention times and sensitivity was made by introducing known gaseous or liquid reagents either through the gas-sampling valve or by direct injection.

Results

Alcohol vapour/Metal Oxide interactions in static system: Mass spectrometric analysis established that no detectable dehydration or dehydrogenation product was evolved into the gas phase at room temperature whenever ethanol, isopropanol or isobutanol contacted vacuum-activated TiO_2 or ZnO. However, contact of t-butanol with ZnO at 10 $N\ m^{-2}$ for 30 min produced measurable isobutene product, which evolved into the gas phase at room temperature and was collected in a trap at $-196^{\circ}C$. Amount of this product is indicated in Table I. Appearance of a measurable alkene product only from the tertiary alcohol appeared consistent with its greater ease of dehydration.

The possibility that other dehydration or dehydrogenation products had been produced from the alcohols by active sites on ZnO or TiO_2 but retained as adsorbed species at room temperature, was investigated by subsequent thermal desorption in vacuo. A liquid N_2 cooled trap was used to collect all condensible species desorbed by increasing the temperature of the metal oxide to $350^{\circ}C$ in 50-degree increments. Results of these thermal desorption studies were conveniently summarised by histograms, such as are shown in Fig. 1a and 1b for various product from isopropanol/ZnO and ethanol/ZnO, respectively. The alkene released at lower temperatures ($30-250^{\circ}C$) is listed in Table I as corresponding to desorption of molecules already formed by alcohol interaction with active sites at room temperature, whereas dehydration product released at higher temperatures ($250-350^{\circ}C$) is attributed to dehydration of strongly-held alcohol during incremental heating of the substrate. Formation of dehydration product on ZnO and TiO_2 surfaces at temperatures $> 250^{\circ}C$ has previously been reported.[8]

No evidence was here obtained for other products from any of the alcohol/metal oxide systems thus studied in a static reactor with subsequent thermal desorption. This argued against formation of long-lived carbonium-ion intermediates in formation of the observed alkenes, since contact times (up to 4 hr) and surface coverage by alcohol (ca. 1% monolayer) appeared adequate to allow for ether formation by bimolecular interaction of alcohol[3] with any such surface carbonium-ion intermediates. These experiments did, however, yield evidence for dehydrogenation of ethanol to acetaldehyde and of isopropanol to acetone, although neither product desorbed at room temperature. Molecular hydrogen fragment in corresponding amount desorbed from ZnO at 50-150°C and from TiO_2 at 150-250°C, followed by acetone from isopropanol (250-350°C) or t-butanol. Contrary to observations reported by McArthur and Bliss,[9] acetaldehyde did not desorb from ZnO but was degraded to propane, methyl acetylene, 1.3 butadiene and CO_2, thermal desorption of which provided indirect evidence for slight dehydrogenation of ethanol on ZnO. Acetaldehyde plus these decomposition products desorbed from TiO_2 in the range 150-350°C. Table I summarises the estimates thus obtained for the extent of room temperature dehydration and dehydrogenation of alcohols over vacuum activated ZnO and TiO_2. Entries in parentheses in the table indicate any marked changes which addition of N_2O at 10 N m^{-2} produced in amount of dehydration or dehydrogenation product when simultaneously admitted with alcohol vapour to the same surfaces and these data demonstrate, in general, enhanced conversion to dehydrogenated product.

Alcohol vapour/Metal Oxide interactions in dynamic systems at pressures < 10^{-2} N m^{-2}: Possibilities for readsorption of primary products and their conversion to other species by secondary reactions on the surface (e.g., oxidation of alkene to aldehyde or ketone by oxygen from the lattice) was an evident disadvantage of the static system. Interactions were, therefore, also studied in dynamic conditions at such low pressures, that, once desorbed, the primary products had comparable probability for readsorption or for condensation into a trap at $-195^{\circ}C$. Subsequent stepwise release of condensed products by warming first to -78° and then to higher temperatures using appropriate refrigerant baths was shown to result in sensitivity adequate to detect acetone or propene products arising from very much lower exposures to isopropanol vapour (0.1 Langmuir) than with the static system (typically 150 Langmuir). Even at this enhanced sensitivity no evidence was found for ether products from any C_2-C_4 alcohol, but this was hardly surprising since probability of two-step processes requiring successive interactions with two alcohol molecules would be very low at the reduced pressure.

Data presented in Part B of Table I facilitate comparison of rates of formation of various products from primary, secondary or tertiary butanols in these conditions over dark or uv-illuminated ZnO and TiO_2. Rather surprisingly these data establish that acetone was the major product from non-illuminated t-butanol/metal oxide interfaces, rather than the isobutene anticipated on the basis of known ease of t-butanol dehydration. These observations, and the absence of measurable isobutene or acetone product from the other butanol/metal oxide systems (cf. Table IB), suggested secondary oxidation of primary isobutene product from t-butanol by oxygen from the non-illuminated metal oxide surfaces.

Entries in parenthesis in Table IB show that illuminating the t-butanol/TiO_2 interface with photons of wavelength > 300 nm greatly enhanced the yield of isobutene without increasing acetone yield. Illumination did not produce detectable yields from isobutanol/TiO_2, but butenes and methyl ethyl ketone photoproducts were readily detected from sec-butanol/TiO_2. Comparison of the yields of butenes from the butanols over illuminated TiO_2 shows that the intrinsic reactivities of the alcohols for loss of H_2O remained important in determining extent of dehydration over the uv-illuminated TiO_2 surface.

Rate of conversion of alcohol vapour to dehydration or dehydrogenation products over non-illuminated TiO_2 or ZnO surfaces in dynamic conditions at room temperature was too slow (typically 1% to acetone and 0.5% to isobutene for t-butanol/ZnO in 30 mins) to permit meaningful monitoring by an on-line mass analyser. We established however, that additional changes produced by continuous uv-illumination of the interfaces could be monitored in this manner and Figure 2a summarises observations made on the t-butanol/ZnO system when illuminated by light transmitted to the interface via. a 38A filter. Note the contrast in this figure between initial rapid evolution of acetone photoproduct into the gas phase and slower appearance of isobutene photoproduct when the t-butanol/ZnO interface was continuously illuminated with a constant flux of photons of wavelengths 340-640 nm. This latter observation suggested either that isobutene was the product of a secondary process on the illuminated interface, or that initial isobutene photoproduct underwent immediate oxidation to acetone until the active oxidation sites became depleted. No acetone or butene photoproducts were detected when sec-butanol and isobutanol, present over ZnO at 10^{-4} N m^{-2}, were uv-illuminated and monitored in identical conditions - an observation which indicated that the intrinsic ease of dehydration of the alcohols was the main rate-determining factor even in photodehydration. Isobutanol and sec-butanol did undergo photoassisted dehydrogenation to isobutyraldehyde and methylethyl ketone and those products increased with illumination time in manner similar to isobutene under illumination 340-640 nm.

The lower trace in Fig. 2b illustrates growth of another dehydrogenation product *viz.* acetaldehyde from the Ethanol/ZnO interface but under illumination by photons at 254 nm. The upper trace in Fig. 2b shows that an increased extent of dehydrogenation was directly observed over this illuminated interface when nitrous oxide was added to the inlet gas at pressure equal to that of alcohol, thereby demonstrating greater sensitivity for this technique than for the static system. Since ESR results reported by Lunsford demonstrated that presence of N_2O over illuminated ZnO greatly enhanced the formation of O^- radicals on this metal oxide, the increased photo-dehydrogenation here directly observed in the presence of N_2O (cf. Fig. 2b) suggests that photogenerated O^- radicals contributed to dehydrogenation at the Ethanol/ZnO interface. Presence of N_2O did not increase dehydration product significantly in these systems when studied with the on-line analyser.

Interactions in Liquid Alcohol/Metal Oxide Systems: Gas chromatographic analysis of vapours carried out of suspension of ZnO or TiO_2 in purified isobutanol by a continuous flow of nitrogen carrier gas established that no significant sustained growth of butenes or isobutyraldehyde or acetone could be achieved either in the dark or under uv-illumination. Visual observation showed that TiO_2 became blue in such conditions, thereby indicating reduction of the TiO_2 surface through photoassisted interaction with the liquid alcohol. Use of oxygen as carrier gas capable of re-oxidising the surface was therefore indicated. With O_2 as carrier gas no significant growth of butenes, isobutyraldehyde, ether or acetone product occurred either in the liquid phase of the non-illuminated suspension or in the vapour phase above it. When illumination commenced, isobutyraldehyde and acetone photoproducts increased steadily over a 400 min period to the limiting values summarised in Part C of Table I. No ether product was detected from isobutanol and ethanol at 20°C or t-butanol at 30°C. For this latter system acetone was the dominant product and no significant growth of isobutene photoproduct was observed but this would be consistent with immediate oxidation of primary isobutene product at the oxygenated interface prior to its release as acetone. When isobutene vapour was admixed with O_2 carrier gas and passed through an illuminated isobutanol/TiO_2 suspension, no significant conversion of isobutene to acetone was detected but this observation could be understood if gas-phase isobutene, unlike that formed by alcohol dehydration, never resided on the metal oxide surface.

Discussion

Efficient abstraction of α-hydrogen by O^- from alcohols has been reported in homogeneous systems[5,6] and other workers have shown that dissociation of N_2O or ZnO results in formation of surface O^- radicals. Consequently, it is reasonable to interpret our observations of added dehydrogenation product at (Alcohol + N_2O)/Z interfaces as evidence for involvement of surface O^- fragments (from N_2O dissociation) in dehydrogenation of adsorbed alcohol. Such surface O^- species would be coordinatively unsaturated and there is some evidence, at least for ZnO surfaces, for their involvement in equilibria of type

$$O^{2-}_{cus} \underset{}{\overset{+h}{\rightleftharpoons}} O^- \overset{+h}{\rightleftharpoons} O_{cus}$$

The success of our sensitive on-line mass analysis in detecting additional dehydrogenation of primary and secondary alcohols at uv-illuminated Alcohol/ZnO interfaces is consistent with formation of additional surface O^- by photogenerated holes in accordance with such equilibria. A corollary of this description of active surface oxygen sites is that these cannot be involved in dehydration of primary or secondary alcohol, since extent of their dehydration was not enhanced by illumination, even on the sensitive on-line analyser, whereas additions of N_2O in the static system reduced the amount of dehydrated product (see Table I). Synchronous loss of OH and H by adjacent carbon atoms at metal-ion, Lewis-acid sites[10] is preferred to carbonium ion formation as the mechanism of dehydration, since no ethers were found.

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Captions to Figures

Figure 1. Histograms illustrating thermally assisted desorption of various products from ZnO surfaces after exposure to alcohols at 20°C.

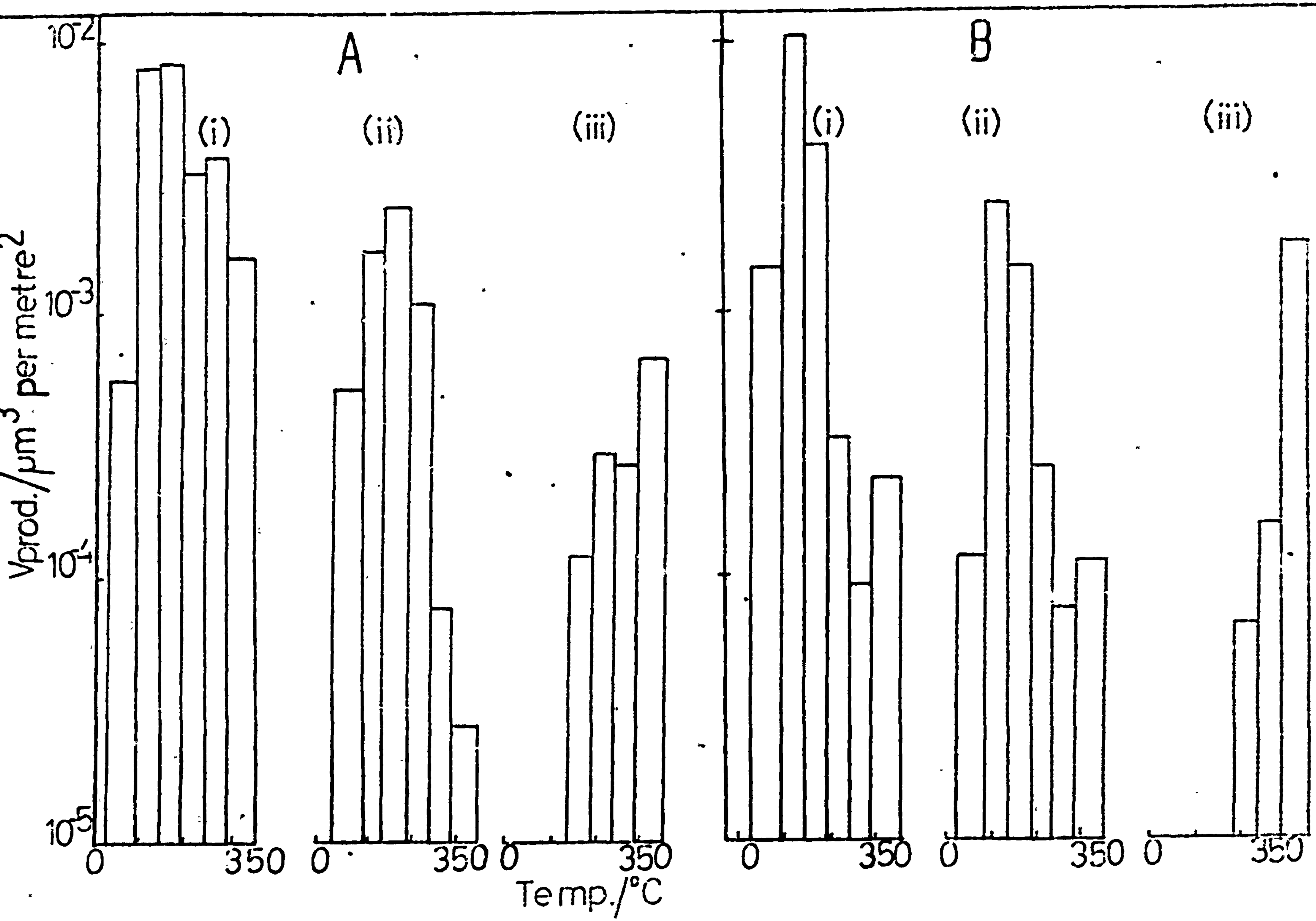
1A Products from Ethanol:
(i) $H_2(g)$ product; (ii) ethylene; (iii) secondary products attributed to acetaldehyde product.

1B Products from Isopropanol:
(i) $H_2(g)$; (ii) propene; (iii) acetone.

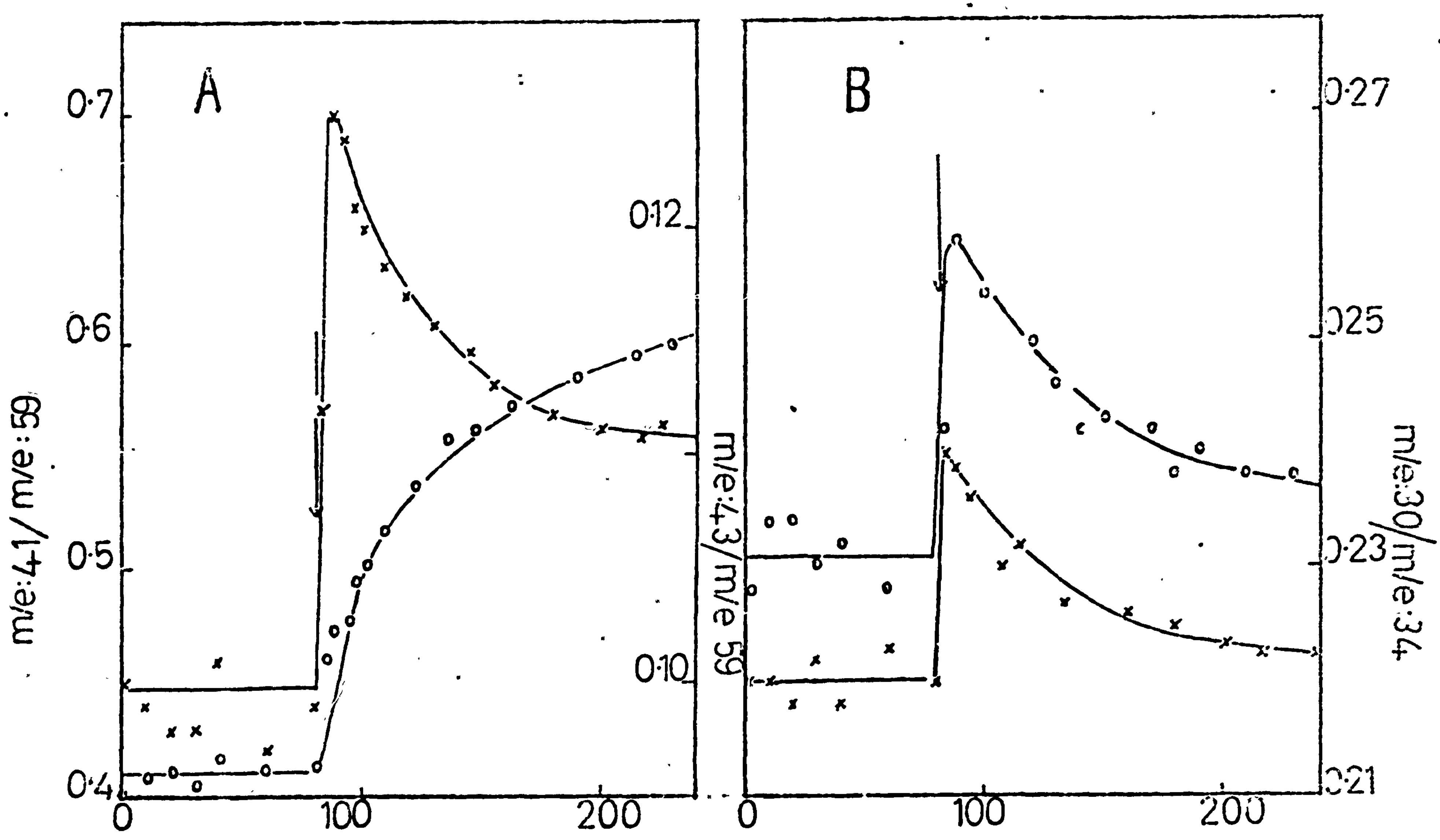
Figure 2. Growth of various photoproducts evolved at 20°C from ZnO/Alcohol interfaces, as monitored by an on-stream Micromass 6 analyser.

2A Photoproducts from t-butanol/ZnO:
upper trace, acetone formation; *lower trace*, isobutane formation.

2B Photoproducts from Ethanol/ZnO:
upper trace, acetaldehyde from C_2D_5OD, *lower trace*, acetaldehyde from (C_2D_5OD + N_2O).



A
B
(i)
(ii)
(iii)
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Vprod./µm³ per metre²
0
350
Temp./°C


A
B
m/e:41/m/e:59
m/e:43/m/e 59
m/e:30/m/e:34
0·7
0·6
0·5
0·4
0·12
0·10
0·27
0·25
0·23
0·21
0
100
200

Dehydration ($-H_2O$) and Dehydrogenation ($-H_2$) Products from Room Temperature Interactions of C_2-C_4 alcohols with ZnO and TiO_2

Part A - Products from Static System: Alcohol Vapour/Metal Oxide

Oxide	Alcohol	Desorp Temp. °C	a ($-H_2O$)	a ($-H_2$)	Other Product
ZnO	t-butanol	20	5.8×10^{-5}	–	–
"	"	20-190	1.6×10^{-2}	–	–
TiO_2	"	20-240	8.1×10^{-2}	–	–
TiO_2	ethanol	20-240°	1.9×10^{-2}	1.3×10^{-3}	5.9×10^{-4}
"	(EtOH + N_2O)		(5.8×10^{-3})	(3.0×10^{-3})	2.3×10^{-4}
ZnO	ethanol	20-190	4.7×10^{-3}	b 1.4×10^{-3}	1.7×10^{-2}
"	(EtOH + N_2O)	"	(3.2×10^{-3})	b (2.6×10^{-3})	1.4×10^{-2}
					$H_2(g)$

Part B - Products from Dynamic System: Alcohol Vapour/Metal Oxide

TiO_2	isobutanol	20°C	$< 2 \times 10^{-3}$	–	–
" + uv	"	"	$< 2 \times 10^{-3}$	–	–
ZnO	"	"	$< 2 \times 10^{-3}$	$< 10^{-3}$	–
ZnO + uv	"	"	8×10^{-3}	$< 10^{-3}$	–
TiO_2	sec-butanol	20°	$< 2 \times 10^{-3}$	$> 10^{-3}$	–
TiO_2 + uv	"	"	$(< 8 \times 10^{-3})$	2×10^{-2}	–
TiO_2	t-butanol	30°	$< 2 \times 10^{-3}$		9×10^{-3}
TiO_2 + uv	"	"	2.4×10^{-2}	–	"
ZnO	"	"	3×10^{-3}	–	5×10^{-3}
					Acetone

Part C - Products from Dynamic System: Liquid Alcohol/Illuminated Metal Oxide

TiO_2	t-butanol	30°	–	–	59.3×10^{-2}
ZnO	"	"	–	–	7.4×10^{-2}
TiO_2	isobutanol	20°	–	28.3×10^{-2}	12.9×10^{-2}
ZnO	"	"	–	23.4×10^{-2}	2.8×10^{-2}
					Acetone

a. Normalised to um^3 of gas phase product (STP) per m^2 of oxide surface per hour

b. Was not evolved until temperatures 250-350°C

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20. Abstract

Migration of energy from irradiated semiconducting solids to acceptor molecules in contact with the solid surface has been experimentally examined and models have been developed to account for the extent-of-reaction, kinetics and selectivity observed. Fast-detection techniques have been developed to follow, on a time-scale of milliseconds, the kinetics of 'fast' processes initiated at semiconducting metal oxide surfaces by UV-illumination and studies included examination of interfaces between Metal Oxides and Aqueous Electrolytes by ESR, plus the study of Metal Oxide/GAS interfaces by a Dynamic Mass Spectrometric technique. Very low quantum efficiencies were measured for photoassisted processes involving adsorption, desorption or reaction of gases at the flash-illuminated surfaces.

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