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HYDROCARBON CHEMISTRY AND CHEMILUMINESCENCE IN HIGH ALTITUDE PLUMES

R. H. Kummler, et al

Physical Dynamics, Incorporated

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by

R. H. Kummler
E. R. Fisher
F. P. Boynton

PHYSICAL DYNAMICS, INC.

P.O. Box 604
College Park Station
Detroit, Michigan 48221

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ABSTRACT

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INTRODUCTION

When significant amounts of unburned or incompletely reacted hydrocarbons are present in the exhaust gases of a rocket engine, chemical reactions between these fuel species and atomic oxygen or OH may lead to substantial IR, visible and UV chemiluminescence from the mixing region. This work represents an attempt to describe the processes leading to emission in terms of a "lumped-parameter" approach for an assumed critical path to the radiating species based on a review of all potentially important processes. The intent of this report is to provide a "baseline" model to the Plume Physics community. At present, we have only begin to examine the model's behavior in plume flows, and the model should be regarded as a working hypothesis in the process of being tested. The focus is predominantly upon IR chemiluminescence; however, many of the same reactions may be involved in visible and UV chemiluminescence, and we indicate how the scheme might be extended to include these processes. No information regarding the actual quantity of unburned hydrocarbons nor the concentration distribution of the various possible species is presently available. Hence, we are concerned herein only with the speculation that at least some trace amounts are present.

The fact that carbon, hydrogen, and oxygen atoms can form a very large number of different compounds is well known. Although the ultimate products in an excess of oxygen are

CO_2 and H_2O, any single hydrocarbon molecule can give rise to a large number of intermediate species along the way. In addition to the attack of O, OH, and O_2 on the original species and its degradation products, many reactions can occur among the intermediate species to create new hydrocarbon species and partially oxidized compounds such as aldehydes, ketones, ethers, and so on. One recent attempt to describe the oxidation of a large hydrocarbon molecule employed a system of 250 reactions screened from an initial list of 1500 (Bahn, 1968).

The modelling studies being conducted under the ARPA Plume Physics Program generally require that a computer code be applied to several different flow and altitude situations and that the sensitivity to input parameters be established. Thus, a moderately large number of runs must be expected. The flow fields to which the hydrocarbon model must be applied are diffusive and therefore reaction expressions must be integrated along many different streamlines. In order to keep the length of the calculation within reasonable limits, the number of reactions included must be minimized. Fortunately, it appears that under conditions prevailing in the mixing region of high-altitude exhaust plumes a reasonable chemical reaction scheme can be developed.

While it is not our purpose to review in detail the available work on hydrocarbon combustion (several recent reviews are available; i.e., Franklin, 1967; Gaydon and Wolfhard, 1970; Herron, 1969; Kondratiev, 1972), a short discussion of some features of the process is necessary to set the stage for the final model. At temperatures below about 500°K, mixtures of hydrocarbons and molecular oxygen react very slowly. At somewhat higher temperatures, reaction rates increase and a number of oxygen-containing products are formed. Complex hydrocarbons mixed with atomic oxygen often exhibit "cool flames," light-emitting reactions which proceed without the intense energy generation characteristic of high-temperature reactions. The products include CO, H_2O, and various aldehydes and peroxides. At high temperatures, reactions are rapid. In excess oxygen, the combustion products are mainly H_2O and CO_2; in very fuel-rich mixtures, or particularly in diffusion flames where rich and lean regions may both exist, a variety of hydrocarbons and partially oxygenated species may be produced.

Considerable effort has been expended upon attempting to understand hydrocarbon combustion under these conventional conditions. Much of the older work has been documented in the various Symposia on Combustion. Examples of more recent efforts include the analysis of cool flame ($\sim$ 700°K) combustion of large branched chain hydrocarbons by Barat, et al (1971) which shows that the predominant products of such oxidation will be alkenes, higher aldehydes and ketones, along with the predominant carbon containing compound, CO. The total carbon in organic (non-CO/CO_2) form was three times that found in inorganic compounds.

The general results of Barat, et al (1971) were confirmed by Knox and Kinnear (1971) for the combustion of fuel rich pentane up to nearly 700°K to form pentene, acetaldehyde, and ketones as the primary HC-oxygen products.

Fish and Wilson (1971) studied the oxidation of 2,3 dimethylbutane up to 550°K; they found butene, lower alkenes, ketones, and alcohols as the major products, along with minor amounts of aldehydes including formaldehyde in mixtures of $HC:O_2 = 1:2$. Subsequent oxidation of the higher aldehydes, as shown by Baldwin, et al (1971) will produce olefins and CO. A review of hydrocarbon combustion processes, based upon work up to about 1966, has been made by Franklin (1967).

MAJOR REACTIONS IN HIGH ALTITUDE HYDROCARBON PLUMES

The tendency to produce hydrocarbon fragments occurs in mixtures of hydrocarbons with air or molecular oxygen at moderate pressures. While conditions in a high-altitude exhaust plume differ significantly from those to which most previous results are applicable, they are in the direction reinforcing the studies cited. Not only is the pressure much lower, so that the three-body recombination reactions are unimportant, but the atmosphere consists in large part of atomic oxygen, which reacts with many hydrocarbons over a wide range of temperatures. In normal combustion vessels, initiation is believed to occur by the process

$$R\text{-}H + O_2 \longrightarrow R\cdot + HO_2$$

which has an activation energy of the order of 50 kcal/mole. In fully developed propagating flames, it appears that initiation on the low-temperature side involves OH diffusing from the reaction zone:

$$R\text{-}H + OH \longrightarrow R\cdot + H_2O \quad .$$

In the plume above 100 km, these processes are replaced by processes involving O atom attack on olefins or on secondary hydrogens in saturated aliphatic hydrocarbons:

$$R\text{-}H + O \longrightarrow R\cdot + OH$$

$$R{=}CH_2 + O \longrightarrow RH\cdot + CHO \quad .$$

On the exhaust-rich side of the mixing layer, temperatures are generally low (200-300°K) and reactions are expected to be very slow. As a hydrocarbon molecule penetrates into the mixing zone, the temperature increases and so does the concentration of O. In the exhaust of an efficient engine, hydrocarbons are not present in large proportions. (The exhaust gases in the nose region of the plume may be an exception because of the influence of cooled walls or peripheral flows of low O/F ratio.) Once in the mixing zone, a hydrocarbon molecule (or a fragment produced by previous reaction) is much more likely to collide and react with an oxygen atom than with other hydrocarbon fragments. As a result, many of the polymerization and fractionation reactions which would occur in a laboratory explosion vessel are much less important in the exhaust plume. Therefore, modelling studies should concentrate on reactions with O and with the OH that is formed by the initial O attack.

Even with this simplification, many complications arise. Let us consider the oxidation of a long-chain aliphatic hydrocarbon in a system containing large amounts of O and OH. (Since olefinic hydrocarbons are produced as intermediate products of oxidation of alkane compounds, we lose no generality by beginning the sequence with the alkane.) The initial attack by O results in hydrogen atom abstraction according to:

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 + O \longrightarrow R_1\text{-}\dot{C}H\text{-}CH_2\text{-}R_2 + OH \quad . \qquad \text{(I)}$$

A significant concentration of OH is produced by this reaction so that H atom abstraction can also occur via OH attack:

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 + OH \longrightarrow R_1\text{-}\dot{C}H\text{-}CH_2\text{-}R_2 + H_2O \qquad \text{(II)}$$

where R_1 and R_2 are H atoms or hydrocarbon radicals. The attack proceeds preferentially on secondary (as shown) or tertiary hydrogen atoms [Herron and Huie (1969)], although the reaction of OH with ethane is also reasonably fast. Reaction (I) is nearly thermoneutral or mildly exothermic, so that the OH produced is not vibrationally excited. Reaction (II) generally liberates enough energy to excite the first or second level of the ν_1 or ν_3 mode of H_2O; some of this energy could also go into exciting the ν_2 mode of H_2O or into vibrational excitations of the alkyl radical. However, the new bond is formed in H_2O and hence it is most probable that the H_2O so formed will be vibrationally excited and that some of the reaction energy will be deposited in each mode.

The radicals produced in Reactions (I) and (II) could react with other hydrocarbon molecules; however, in the presence of excess O or OH, they will most probably react with O or OH. The products of these combinations are not established. We suggest two potential routes, the first of which is:

$$R_1\text{-}\dot{C}H\text{-}CH_2\text{-}R_2 + O \longrightarrow R_1\text{-}CH{=}CH\text{-}R_2 + OH \qquad \text{(III)}$$

or

$$R_1\text{-}\dot{C}H\text{-}CH_2\text{-}R_2 + OH \longrightarrow R_1\text{-}CH{=}CH\text{-}R_2 + H_2O\ . \qquad \text{(IV)}$$

In either of these reactions, the energy released is very large (60 to 80 kcal/mole), and considerable excitation of the product molecules can be expected. If the radical is a long-chain molecule, the O or OH may attack the molecule as in reaction I or II at other places along the chain. In general, one expects III or IV to be a faster process and, unless the chain is very long, to represent the preferred reaction path for the disappearance of the radicals. No direct experimental data are available for radical plus O and OH reactions, but we expect Reactions III and IV to have rate constants approaching gas kinetic.

The olefins produced in Reactions III and IV will react rapidly with O to give an aldehyde radical and an alkyl radical:

$$R_1\text{-CH=CH-}R_2 + O \longrightarrow R_1\text{-}\dot{C}H_2 + R_2\dot{C}O \quad . \qquad \text{(V)}$$

The reactions of OH with olefins have been less well studied, but appear to produce aldehydes [Morris, et al (1971)] with the release of a hydrogen atom for the smaller olefins, and presumably an alkyl radical for the larger olefins:

$$R_1\text{-CH=CH-}R_2 + OH \longrightarrow R_2\cdot + R_1\text{-CH}_2\text{-CHO} \quad . \qquad \text{(V}')$$

Neither (V) nor (V′) represents the sole process occurring as the result of O or OH attack. In either case it is possible and probable [Kanofsky, et al (1972)] that other radicals will be formed. However, as we have suggested, the basic arguments are unchanged by these possibilities. Here again energy is released so that we may expect excitation of the products. The alkyl radical now repeats the processes illustrated in steps III and IV. The aldehyde radical can undergo a number of different reactions including hydrogen abstraction and CO formation. It is at this point of the process that things begin to get complicated, and a set of simplifying assumptions is introduced.

Note that the set of processes up through V tend to produce alkyl radicals with the unpaired electron near one end of the chain. In general, movement of this electron to a different position (carbon) on the chain (and movement of an H atom to compensate) will require some activation energy which must be supplied by collisions. We shall hypothesize that this process is slow, except across a double bond, and that the unpaired electron is relatively immobile. Then, after one cycle of degradation by processes I-V, the succeeding version of reaction III or IV will result in a double bond at one end of the chain:

$$R_1\text{-}\dot{C}H_2 + \left\{\begin{matrix} O \\ OH \end{matrix}\right\} \longrightarrow R_3\text{-}CH{=}CH_2 + \left\{\begin{matrix} OH \\ H_2O \end{matrix}\right\} \qquad \left\{\begin{matrix} \text{(IIIa)} \\ \text{(IVa)} \end{matrix}\right\}$$

Oxygen atoms attacking this olefin will produce the formyl radical

$$R_3\text{-}CH{=}CH_2 + O \longrightarrow R_3\text{-}\dot{C}H_2 + HCO \quad . \qquad \text{(Va)}$$

The new radical ($R_3 - \dot{C}H_2$) then continues the cycle until the number of carbon atoms is reduced to two, while the formyl radical reacts in a very exothermic process to form CO and OH:

$$HCO + O \longrightarrow CO + OH \quad . \qquad \text{(VI)}$$

The OH so formed is almost certainly vibrationally excited (Krieger, Malki and Kummler, 1972). The C_2 olefin (ethylene) which eventually results from this degradation process is consumed by reaction with either O or OH to form a methyl radical and formyl or formaldehyde:

$$C_2H_4 + O \longrightarrow CH_3 + HCO \qquad \text{(VII)}$$

$$C_2H_4 + OH \longrightarrow CH_3 + CH_2O \quad . \qquad \text{(VIII)}$$

Herron and Penzhorn (1969) concluded on the basis of isotope flow tube studies and product yields that the primary product of the O + C_2H_4 is not H_2CO. However, Westenberg and deHaas (1969) argue on the basis of their H_2CO mass spectrometric measurements that formaldehyde is a primary product. Niki, Daby and Weinstock (1969) agree with Herron on the basis of their independent isotopic ethylene experiments. The high intensity crossed beam results of Kanofsky, et al (1972) show by direct examination of the products in a collision-free environment, that the major products (90%) are definitely CHO + CH_3 in accord with the original suggestion of Cvetanovic (1963). In addition, CHO is found as a major product in the oxidation of higher olefins as well. Hence, in Figure 1, we symbolically simplify the actual attack of O on C_nH_{2n} to

$$O + C_nH_{2n} \longrightarrow \cdot C_{n-1}H_{2n-1} + CHO \, .$$

Several possibilities exist for the reaction of the methyl radical, produced in this sequence, including O atom attack and reaction with higher hydrocarbons. We hypothesize that in the oxygen-rich plume environment the dominant processes will be reaction with O and O_2 to form H, OH and formaldehyde, as in the oxidation of methane at low temperatures (see, e.g., Franklin, 1967):

$$CH_3 + O_2 \longrightarrow CH_2O + OH \tag{IX}$$

or

$$CH_3 + O \longrightarrow CH_2O + H \, . \tag{IXa}$$

A series of further two-body reactions completes the oxidation process:

$$CH_2O + O \longrightarrow HCO + OH \tag{X}$$

$$CH_2O + OH \longrightarrow HCO + H_2O \tag{XI}$$

$$OH + O \rightleftarrows O_2 + H \tag{XII}$$

$$OH + CO \rightleftarrows CO_2 + H \tag{XIII}$$

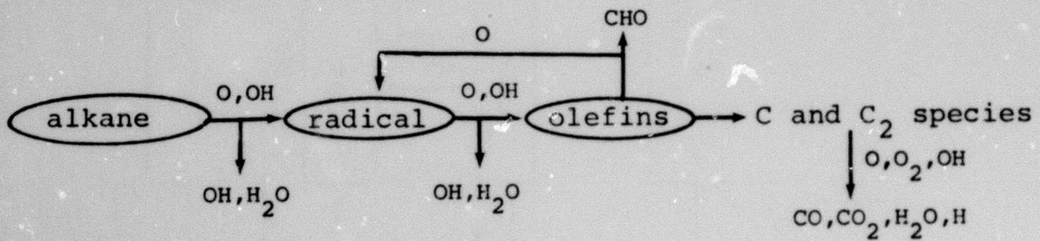
$$OH + H_2 \rightleftarrows H_2O + H \tag{XIV}$$

$$OH + OH \rightleftarrows H_2O + O \tag{XV}$$

$$OH + H \rightleftarrows H_2 + O \tag{XVI}$$

THE LUMPED PARAMETER HYDROCARBON CHEMISTRY MODEL

In essence, the assumptions that we have made lead to a model which consists of a cyclic stripping of C_n hydrocarbons to form C_{n-1} hydrocarbons, OH, H_2O, and HCO, followed by a set of reactions which ultimately produce CO, CO_2, H, and more H_2O. All of these reactions are two-body reactions, since three-body collisions are extremely rare at the low densities involved. The cyclic processes, once initiated, take saturated hydrocarbons and convert them to radicals and olefins which react to form more radicals and olefins. Until the number of carbon atoms is reduced to two, the cyclic processes neither create nor destroy radicals or olefin; the process is shown in diagrammatic form below:



This process is shown in more detail in Figure 1. The behavior of C_2 species is different from those of higher hydrocarbons in two respects: first, since ethane has no secondary hydrogens, it reacts with OH rather than with O:

$$C_2H_6 + OH \longrightarrow C_2H_5 + H_2O \quad ; \qquad \text{(XVII)}$$

second, the ethylene reactions VII and VIII break the cycle since the methyl radicals formed here disappear through a different path than the higher radicals formed in Reaction V.

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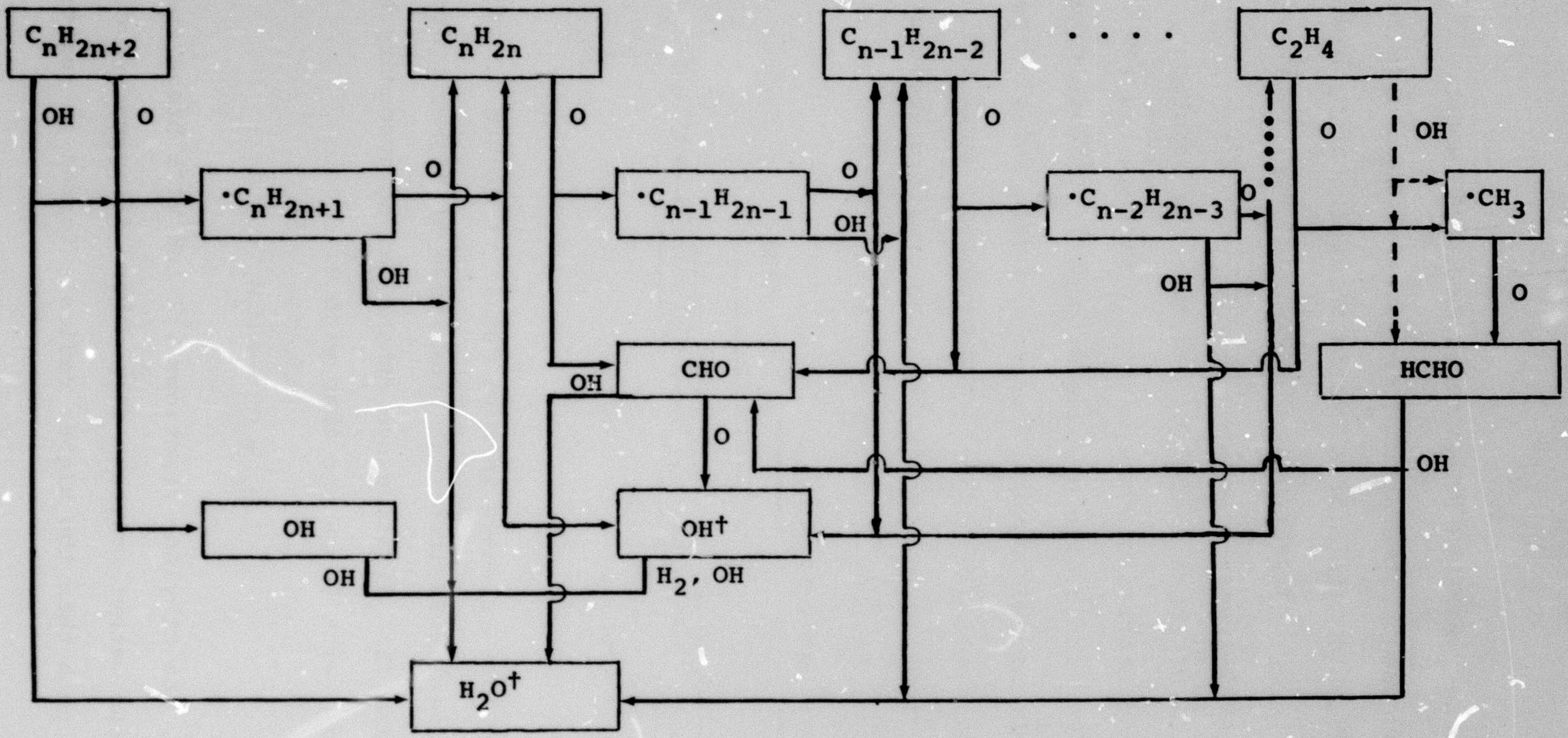

Figure 1a. Simplified flow diagram for low temperature straight chain hydrocarbon combustion. Actual process will also form higher Aldehydes, Epoxides, etc., and will form fragments at the double bond.

The fact that the production of alkyl radicals and olefins cycles from high to low carbon number with the same kind of reactions taking place in each cycle makes it possible to adopt a "lumped-parameter" model in which all species with more than two carbon atoms are classed together as alkanes, radicals, or olefins, and the reactions of all species in each of these classes are treated together with an average rate coefficient (see Appendix IV for a comparison of the available data and the lumped parameter rate constants). The connection between the long-chain cyclic processes and C_2 hydrocarbon formation is made by assuming that some fraction of Reaction V produces C_2H_5. With this scheme, we are able to accommodate a variety of initial hydrocarbon compositions in the exhaust gases, together with the other intermediate species such as formaldehyde. Since no reliable measurements or predictions exist for the composition, this is a desirable feature since it allows us to examine the effects of the initial composition (e.g., Appendix III) and subsequently, the sensitivity of the predicted radiant intensity. The precise choice of rate constants for the "lumped" system is made using a conservative rate constant for the rate controlling step and average rate constants for the other processes. The actual data together with the lumped parameter rate constants are given in Appendix IV.

The larger radicals formed in this lumped parameter mechanism can be expected to undergo significant decomposition to aldehydes under attack by O. In fact, this may be the major path for the larger radicals. The equivalent diagram for the decomposition products according to this hypothesis is illustrated in Figure 1b. HCHO would be a major reactant in this scheme and ultimately CHO, $OH^{\dagger}$, and $H_2O^{\dagger}$ would be formed as in Figure 1a. However, a major fraction of the energy would be deposited in RO rather than in OH. Hence H_2O would assume a greater importance since $RO^{\dagger}$ might preferentially decompose instead of radiate. As a first approximation we can assume that the aldehyde scheme does not fundamentally alter the major thrust of the lumped parameter model of Table I.

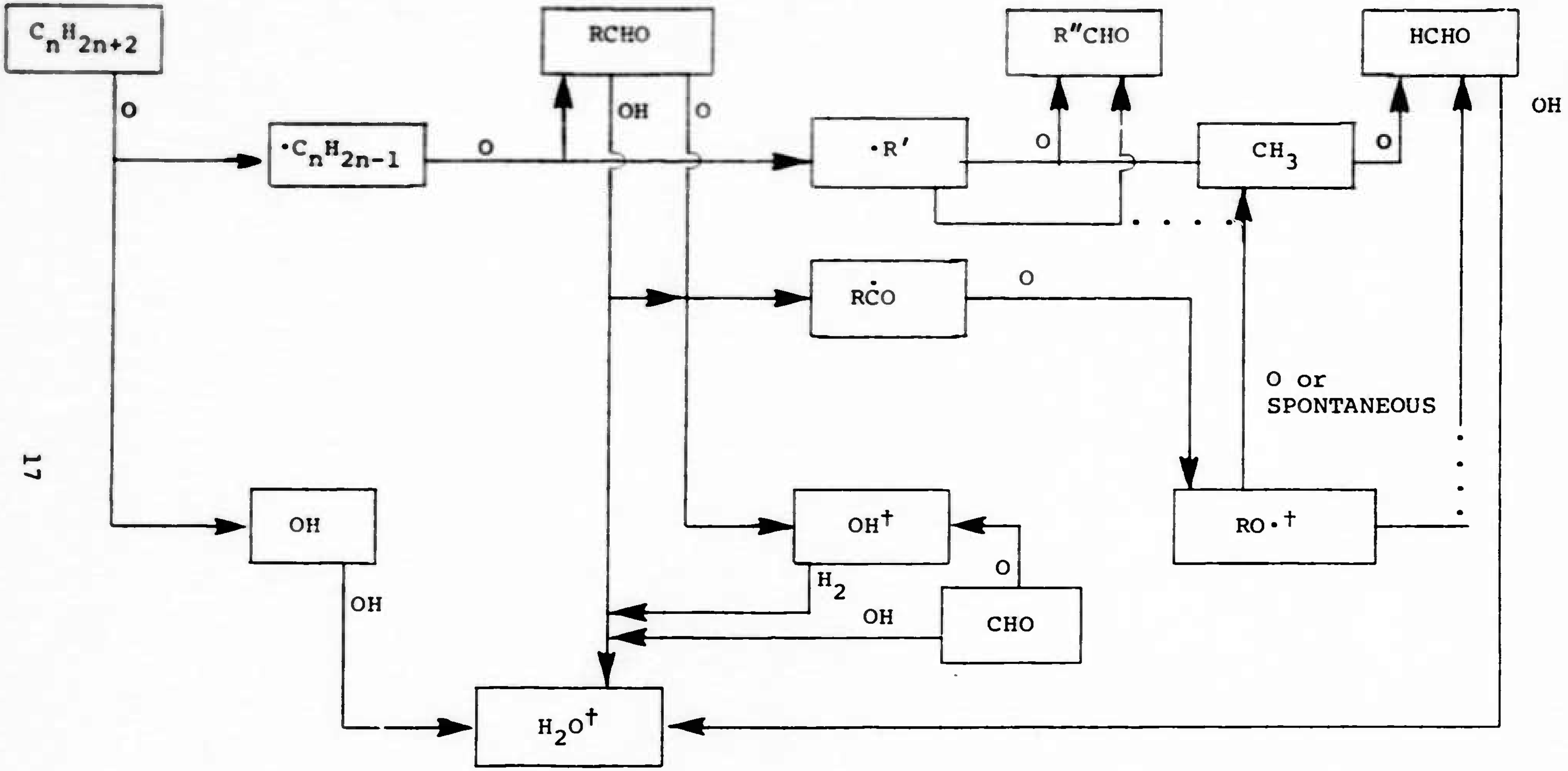

FIGURE 1b. An alternative model for HC oxidation through an aldehyde intermediate mechanism.

TABLE I
LUMPED PARAMETER
IR REACTION SCHEME*

Reaction		Rate Constant, cc/sec	Photon Yield
1.	$A + O \rightarrow R + OH$	$1.3 \times 10^{-10}\ e^{-4840/RT}$	--
2.	$A + OH \rightarrow R + H_2O$	$1.2 \times 10^{-11}\ e^{-850/RT}$	1
3.	$R + O \rightarrow O\ell + OH$	1×10^{-11}	6
4.	$R + OH \rightarrow O\ell + H_2O$	1×10^{-11}	7
5.	$O\ell + O \rightarrow (80\%)\ R + CHO$	1×10^{-11}	--
	$\rightarrow (20\%)\ C_2H_5 + CHO$	1×10^{-11}	--
6.	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$1.8 \times 10^{-11}\ e^{-2480/RT}$	1
7.	$C_2H_5 + O \rightarrow C_2H_4 + OH$	1×10^{-11}	5
8.	$C_2H_5 + OH \rightarrow C_2H_4 + H_2O$	1×10^{-11}	5
9.	$C_2H_4 + O \rightarrow CH_3 + CHO$	$5 \times 10^{-12}\ e^{-1040/RT}$	--
10.	$C_2H_4 + OH \rightarrow CH_3 + CH_2O$	$1 \times 10^{-11}\ e^{+900/RT}$	--
11.	$CH_4 + OH \rightarrow CH_3 + H_2O$	$4.0 \times 10^{-12}\ e^{-5000/RT}$	1
12.	$CH_3 + O_2 \rightarrow CH_2O + OH$	1.7×10^{-13}	1
13.	$CHO + O \rightarrow CO + OH$	5×10^{-11}	8
14.	$CH_2O + OH \rightarrow CHO + H_2O$	$4 \times 10^{-14}\ e^{-1000/RT}$	2
15.	$CH_2O + O \rightarrow CHO + OH$	$1 \times 10^{-12}\ e^{-1000/RT}$	1
16.	$CHO + OH \rightarrow CO + H_2O$	1×10^{-12}	9
17.	$OH + O \rightarrow O_2 + H$	2.2×10^{-11}	--

TABLE I
cont'd

18.	$OH + CO \rightarrow CO_2 + H$	$9.3 \times 10^{-13}\ e^{-1080/RT}$	--
19.	$OH + H_2 \rightarrow H_2O + H$	$3.7 \times 10^{-11}\ e^{-5150/RT}$	1
20.	$OH + OH \rightarrow H_2O + O$	$9.5 \times 10^{-12}\ e^{-780/RT}$	1
21.	$OH + H \rightarrow H_2 + O$	$1.2 \times 10^{-11}\ e^{-7300/RT}$	--
22.	$H + O_2 \rightarrow OH + O$	$3.7 \times 10^{-10}\ e^{-16,800/RT}$	--
23.	$H + CO_2 \rightarrow CO + OH$	$9.3 \times 10^{-11}\ e^{-23,500/RT}$	--
24.	$H + H_2O \rightarrow OH + H_2$	$1.4 \times 10^{-9}\ e^{-20,100/RT}$	--
25.	$O + H_2O \rightarrow OH + OH$	$9.5 \times 10^{-11}\ e^{-18,000/RT}$	--
26.	$O + H_2 \rightarrow OH + H$	$2.9 \times 10^{-11}\ e^{-9450/RT}$	--
27.	$CH_3 + O \rightarrow CH_2O + H$	3.3×10^{-11}	--
28.	$CHO + H \rightarrow CO + H_2$	3.3×10^{-11}	--

"A" is a saturated hydrocarbon, C_nH_{2n+2}, with $n \geq 3$

"R" is an alkyl radical, C_nH_{2n+1}, with $n \geq 3$

"Oℓ" is an olefinic hydrocarbon, C_nH_{2n}, with $n \geq 3$

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* For Literature Citations, see TABLE IV.
For more detail on the lumped parameter rate constants, see Appendix IV.

IR EMISSION

In Table I, we have presented the maximum vibrational level to which the newly formed heteronuclear product molecule can be elevated by each exothermic reaction. All of those noted reactions involving a hydrocarbon or hydrocarbon derivative plus O or OH are potential important sources of infrared radiation. At high altitudes the vibrationally excited molecules are lost primarily through radiative decay. Hence, the exothermicity of the reaction forming the excited state provides an upper limit to the number of photons which would be observed at the fundamental wavelength assuming that sufficient time exists for the cascade down from the maximum level. Not all of the energy of a particular exothermic reaction is necessarily available to the vibrational mode. However, there is experimental evidence for the reaction of the type listed in Table I that a substantial fraction of the energy may be converted into vibrational energy.

Early work by Clough and Thrush (1968) suggested that I.R. chemiluminescence accompanies the oxygen atom attack on both C_2H_4 and C_2H_2, but with quite different mechanisms. They found strong OH emission from

$$O + C_2H_4 \rightarrow \text{products} \quad (\text{up to } v = 3 \text{ OH}) (< 29 \text{ kcal})$$

with H_2CO emission in ν_1 and ν_4 (~ 8 kcal), but only weak CO emission in the fundamental. It was suggested by Clough and Thrush that their findings supported the reaction

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$$O + C_2H_4 \rightarrow CH_3 + CHO$$

as the primary step, rather than

$$O + C_2H_4 \rightarrow CH_2 + HCHO \ .$$

This has indeed been verified by the direct measurements of Kanofsky, et al (1972). In the oxidation of C_2H_4, then, the major source of CO is

$$O + CHO \rightarrow OH + CO \ ,$$

where it is unlikely that the product CO is a new bond. Thus, most of the available energy would be expected to become vibrational energy in the newly-formed OH bond. This is in excellent agreement with the observed evidence of Krieger, Malki and Kummler (1972), as illustrated in Figures 2 and 3.

In the oxidation of acetylene on the other hand, strong CO emission (up to $v = 15$ at 84 kcal) is found by Clough and Thrush which suggests that CH_2 plays a strong role through

$$O + C_2H_2 \rightarrow CO + CH_2 + 48 \text{ kcal/mole}$$

and

$$O + CH_2 \rightarrow CO + 2H + 72 \text{ kcal/mole.}$$

In both cases the CO formed must be a new bond and hence strong CO vibrational emission would be predicted again in agreement with the observation. However, these are not the only products of C_2H_2 combustion (See Table IV).

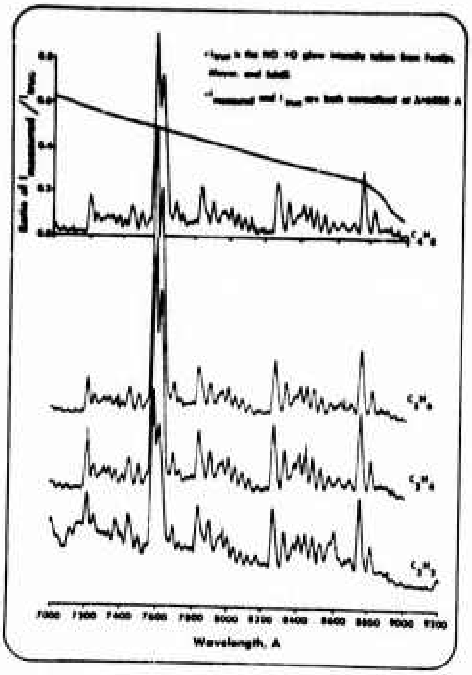

Figure 2. Intensity of chemiluminescence in the 7000–9000Å region from O attack on unsaturated hydrocarbons

Total pressure is 1.28 torr and the hydrocarbon partial pressure is 20 mtorr

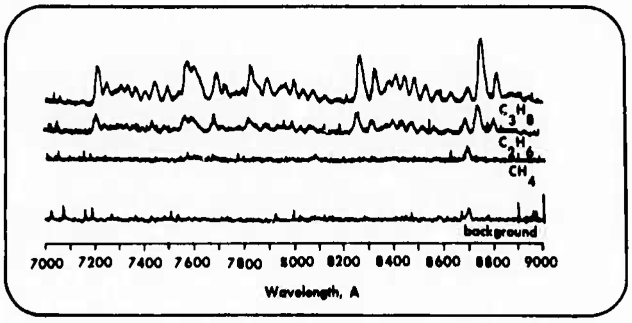

Figure 3 Intensity of chemiluminescence in the 7000–9000Å region from O atom attack on saturated hydrocarbons

Total pressure is 1.28 torr and the hydrocarbon partial pressure is 20 mtorr

Barbara Krieger, Mazen Malki, and Ralph Kummler

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VISIBLE-UV - VACUUM UV LIGHT EMISSION

Some of the oxidation processes in hydrocarbon combustion may produce excited electronic states in the product molecules. Kydd and Foss (1967) have published an elaborate attempt to correlate CH, OH, C_2 and CHO emission spectra from C_2H_2, C_2H_4, C_3H_8 and CH_4 emission in order to establish mechanistic relations. They found that all emissions were uncorrelated. Nonetheless, a wide variety of mechanisms have been suggested to explain the observed emission bands; for example see Table II and also the reviews by Fontijn, et al (1972) and Birely (1973). The mechanisms likely to produce the bands of Table II in the high altitude plume region are shown in Figure 4, and in detail in Table III along with a very tentative set of rate constants for the necessary reactions. This reaction set does not play an important role in the overall combustion process. Therefore it need only be added as a perturbation for a specific attempt to predict visible, UV or VUV radiation. All of the excited electronic state products have very short radiative lifetimes (< 1 μsec) and therefore do not diffuse in the flow field. Moreover their loss rates are always radiatively controlled so that the predicted radiation is independent of the radiative transition probability.

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TABLE II

BAND SPECTRA EMITTED BY FLAMES*

Species	Transition	Name of System	Energy levels,[+] kcal mole^{-1} Upper	Lower	Band head wavelength, Å
OH	$A^2\Sigma^+ \rightarrow X^2\Pi(1,0)$		101.28	0	2811
	$A^2\Sigma^+ \rightarrow X^2\Pi(2,1)$		109.29	10.19	2875
	$A^2\Sigma^+ \rightarrow X^2\Pi(0,0)$		92.75	0	3064
CH	$C^2\Sigma^+ \rightarrow X^2\Pi(0,0)$		90.88	0	3144
	$B^2\Sigma^- \rightarrow X^2\Pi(0,0)$		73.52	0	3872
	$A^2\Delta \rightarrow X^2\Pi(0,0)$		66.25	0	4312[++]
C_2	$d^1\Sigma_u^+ \rightarrow x^1\Sigma_g^+(0,0)$	Mulliken	123.58	0	2325 (headless
	$B^3\Pi_g \rightarrow X^3\Pi_u(0,3)$	Fox-Herzberg	a + 113.81	a + 113.68	2855[++]
	$B^3\Pi_g \rightarrow X^3\Pi_u(0,4)$		a + 113.81	a + 18.10	2987[++]
	$c^1\Pi_g \rightarrow b^1\Pi_u(3,1)$	Deslandres-d'Azambuja	112.45	28.16	3398.1
	$c^1\Pi_g \rightarrow b^1\Pi_u(3,2)$		112.45	32.63	3587.6
	$c^1\Pi_g \rightarrow b^1\Pi_u(0,0)$		97.89	23.64	3852.1
	$A^3\Pi_g \rightarrow X^3\Pi_u(1,0)$	Swan	a + 60.42	a + 0	4737.1
	$A^3\Pi_g \rightarrow X^3\Pi_u(0,0)$		a + 55.42	a + 0	5165.2
	$A^3\Pi_g \rightarrow X^3\Pi_u(0,1)$		a + 55.42	a + 4.64	5635.5
CO	$A^1\Pi \rightarrow X^1\Sigma^+(3,4)$	Fourth positive system	197.52	24.09	1647.8
	$A^1\Pi \rightarrow X^1\Sigma^+(0,3)$		185.11	18.19	1712.2
	$A^1\Pi \rightarrow X^1\Sigma^+(1,4)$		189.35	24.09	1729.5
CN	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(1,0)$	Violet system	79.83	0	3590.4
	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(0,0)$		73.73	0	3883.4
	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(0,1)$		73.73	5.83	4216.0[++]
NH	$A^3\Pi \rightarrow X^3\Sigma(0,0)$		85.10	0	3360
	$A^3\Pi \rightarrow X^3\Sigma(1,1)$		93.80	8.92	3371

[+] a = 1.74 kcal mole^{-1}. [++] Other heads also.

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* After Williams and Smith (1970).

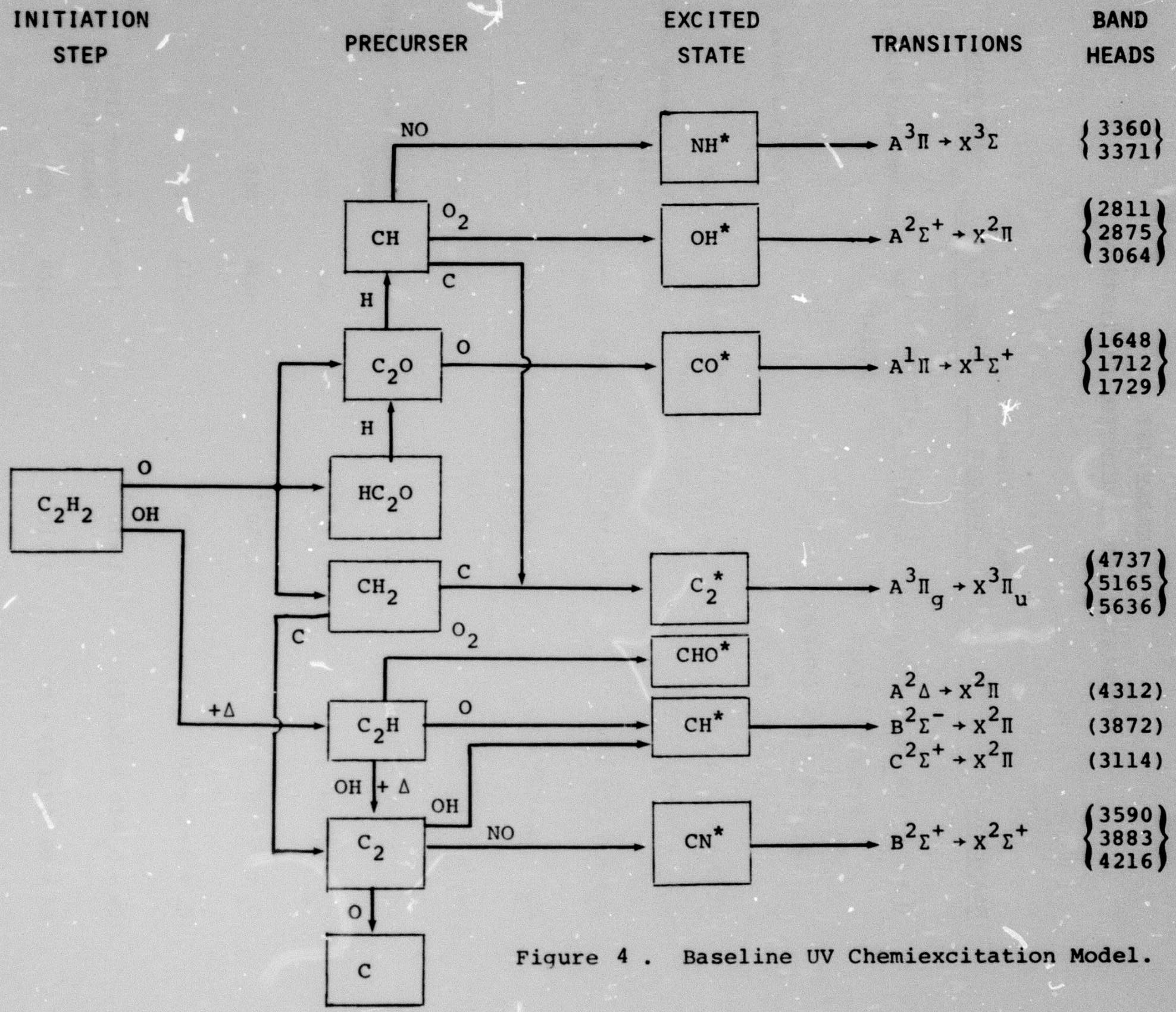

Figure 4 . Baseline UV Chemiexcitation Model.

TABLE III
MECHANISM FOR ELECTRONIC EXCITATION

Reaction	Rate Constant, cc/sec	ΔH_{298} (g.s.)	Reference
$O + C_2H_2 \rightarrow CH_2 + CO$ (15-45%)	$2.4 \times 10^{-11}\ e^{-1780/T}$ (Total)	-48	James and Glass (1969)
$\rightarrow CH_2CO$ (25%)			
$\rightarrow HC_2O + H$ (30-60%)		-23	Jones and Bayes (1964)
$\rightarrow C_2O + H_2$ (0.3%)		-22	
$HC_2O + H \quad C_2O + H_2$	1×10^{-11}	0	EST
$C_2H_2 + OH \rightarrow C_2H + H_2O$	$2.3 \times 10^{-11}\ e^{-3500/T}$	-4.3	Fenimore and Jones (1964)
$C_2O + O \rightarrow CO^* + CO$	1×10^{-10} (all states)	-205	Becker (1969) Shackelford, et al (1972)
$C_2O + OH \rightarrow CH^* + CO_2$	1×10^{-11}	-54.3	EST
$CH_2 + C \rightarrow C_2^* + H_2$	1×10^{-11}	-67.7	EST
$CH_2 + O \rightarrow CO + 2H$	10^{-11}	-76.8	Clough and Thrush (EST)
$C_2 + OH \rightarrow CH^* + CO$	1×10^{-12}	-94	EST
$C_2 + NO \rightarrow CN^* + CO$	1×10^{-12}	-136	EST
$C_2 + O \rightarrow C + CO$	1×10^{-12}	-113	EST
$CH + O_2 \rightarrow CO + OH(A^2\Sigma)$	1×10^{-13}	-159.5	Porter (1967); Smith (1972)
$CH + NO \rightarrow NH(A^3\Pi) + CO$	1×10^{-13}	-109	EST

TABLE III
cont'd

$C_2H + O \rightarrow CH^* + CO$	1×10^{-10}	-60.5 ± 8	Browne, *et al*, est (1969)
$C_2H + OH \rightarrow C_2 + H_2O$	$1 \times 10^{-11}\ e^{-7500/T}$	+15	EST
$C_2H + O_2 \rightarrow HCO^* + CO$	$1.8 \times 10^{-11}\ e^{-3500/T}$	-145	Brown, *et al*, est (1969)
$HC_2O + H \rightarrow C_2O + H_2$	1×10^{-12}	0	Becker,(1969)

SUMMARY

We have outlined herein a plausible simplified mechanism for the oxidation of hydrocarbons under conditions germane to high altitude plumes. We find that in the low pressure, high oxygen atom environment above 100 km, a sequence of bimolecular reactions leading to both IR and UV light emission can be initiated by the oxygen atom attack on secondary hydrogens in saturated hydrocarbons containing more than three carbon atoms as well as by O and OH attack on the unsaturated hydrocarbons which may be present initially or produced in the sequence. The highly exothermic reactions between O and OH with reactive intermediate radicals are prime possibilities for the production of vibrationally excited OH and H_2O respectively. While the detailed mechanism is undoubtedly extremely complex, the sequence basically consists of the conversion of alkanes to olefins to aldehydes in the presence of excess O. A specific set of prototype reactions with rate constants is recommended for the basic chemistry; an upper limit to the IR radiation per reaction based upon the exothermicities of these reactions is suggested; and a UV perturbation mechanism based upon the presence of acetylene is suggested.

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APPENDIX I

A Survey of Oxygen-Carbon-Hydrogen Reactions

In order to determine the appropriate rate constants for the model, we have reviewed the pertinent chemistry and have tabulated the reactions along with measured or estimated rate constants, the standard heat of reaction, and the reference in Table IV. When the product is in an excited state, the appropriate correction must be made, since ΔH_{298}^{R} refers to ground state reactants and products. All rate constants are given in units consistent with concentrations in molecules/cc; ΔH_{298}^{R} is given in kcal/gmole. We have included many reactions which have been suggested to explain laboratory data even when no experimental rate constants have been determined. It should also be recognized that even when experimental data exist the given rate constant expressions cover a limited temperature range, and extrapolation may be needed to apply them to mixing zone conditions. When the authors did not provide the heat of reaction, that data was computed from the heats of formation given in Appendix III.

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TABLE IV

REACTIONS OF HYDROCARBONS AND HYDROCARBONS-OXYGEN-RADICALS WITH O, OH

A. Alkane C_n Reactions ($n \geq 3$)

Reaction	Rate Constant	ΔH^R_{298}	Reference
$C_nH_{2n+2} + O \rightarrow C_nH_{2n+1} + OH$	$k = 8.3 \times 10^{-12}\, e^{-2900/T}\, N_1$ $+ 2.16 \times 10^{-11}\, e^{-2250/T}\, N_2$ $+ 2.66 \times 10^{-11}\, e^{-1650/T}\, N_3$ (N_1 = no. of primary CH bonds in C_nH_{2n+2}, N_2 = no. of secondary CH bonds, N_3 = no. of tertiary CH bonds.)	~0	Herron and Huie (1969)
$C_nH_{2n+2} + OH \rightarrow C_nH_{2n+1} + H_2O$	$k = 1 \times 10^{-12}\, e^{-825/T}\, N_1$ $+ 2.3 \times 10^{-12}\, e^{-430/T}\, N_2$ $+ 2.1 \times 10^{-12}\, e^{+96/T}\, N_3$		Greiner (1970a)
$C_3H_8 + OH \rightarrow C_3H_7 + H_2O$	1.4×10^{-12} (298°K)		Greiner (1967)
	$1.2 \times 10^{-11}\, e^{-678/T}$		Greiner (1970a)

TABLE IV
cont'd

$n\text{-}C_4H_{10} + O \rightarrow C_4H_9 + OH$	$2.8 \times 10^{-11} e^{-2600/T}$		Papadopoulas, *et al* (1971)
	$1.0 \times 10^{-10} e^{-2570/T}$		Herron and Huie (1969)
	1.7×10^{-12}	-23.3	Papadopoulas, *et al* (1971)
$iso\text{-}C_4H_{10} + OH \rightarrow i\text{-}C_4H_9 + H_2O$	2.1×10^{-12} (297°K)	-6.37	Greiner (1967)
	$(3.5 \pm 0.8) \times 10^{-12}$ (298°K)		Gorse and Volman (1972).
$n\text{-}C_5H_{12} + O \rightarrow C_5H_{11} + OH$	$1.3 \times 10^{-10} e^{-2320/T}$		Herron and Huie (1969)
$iso\text{-}C_5H_{12} + O \rightarrow C_5H_{11} + OH$	1.3×10^{-13} (307°K)		Herron and Huie (1969)
$n\text{-}C_6H_{14} + O \rightarrow \cdot C_6H_{13} + OH$	$1.8 \times 10^{-10} e^{-2250/T}$		Herron and Huie (1969)
2,3 Dimethylbutane + $O \rightarrow$	$5.2 \times 10^{-11} e^{-1650/T}$		Herron and Huie (1969)
$n\text{-}C_7H_{16} + O \rightarrow \cdot C_7H_{15} + OH$	$2.0 \times 10^{-10} e^{-2190/T}$		Herron and Huie (1969)

TABLE IV
cont'd

2,2 Dimethylpentane + O → C_7H_{15} + OH	1.0×10^{-13} (307°K)	Herron and Huie (1969)
2,4 Dimethylpentane + O → C_7H_{15} + O	1.7×10^{-13} (307°K)	Herron and Huie (1969)
n-C_8H_{18} + O → C_8H_{17} + OH	$1.5 \times 10^{-10}\ e^{-2030/T}$	Herron and Huie (1969)
3 Methylheptane + O → products	1.1×10^{-13} (300°K)	Ford and Endow (1957)
2,2,4 Trimethylpentane + O → C_8H_{17} + OH	1.2×10^{-13} (307°K)	Herron and Huie (1969)
	5×10^{-14} (307°K)	Herron and Huie (1969)
2,2,3,3-Tetramethylbutane + O → C_8H_{17} + OH	1.4×10^{-14} (307°K)	Herron and Huie (1969)

TABLE IV
cont'd

B. Olefins (C_n, $n \geq 3$)

Reaction	Rate Constant	ΔH_{298}	Reference
$C_3H_6 + O \rightarrow$ products	3.6×10^{-12} (300°K)		Stuhl and Niki (1971)
$\rightarrow C_2H_5 + CHO$		~ -27	Kanofsky, *et al* (1972)
$\rightarrow CH_3 + CH_3 + CO$			" "
	$1.1 \times 10^{-11}\ e^{-515/T}$		Atkinson and Cvetanovic (1972)
	$(4.2 \pm .3) \times 10^{-12}\ e^{-(38 \pm 22)/T}$		Kurylo (1972)
$C_3H_6 + OH \rightarrow$ products $(CH_3 - CH_2 - CHO)$	1.7×10^{-11}		Morris, *et al* (1971)
$1\text{-}C_4H_8 + O \rightarrow$ product	$(1.46 \pm .15) \times 10^{-11}\ e^{-380/T}$		Huie *et al* (1971)
	$1.0 \times 10^{-11}\ e^{-405/T}$		Atkinson and Cvetanovic (1972)
$2\text{-}C_4H_8 + O \rightarrow C_2H_3O + C_2H_5$			Kanofsky, *et al* (1972)
$\rightarrow C_3H_5O + CH_3$			
$\rightarrow CHO + C_3H_7$ (minor)			
Trans-2-butene + H → products	1×10^{-12}		Braun and Lenzi (1967)

TABLE IV
cont'd

iso-$C_4H_8 + O \rightarrow CHO + C_3H_7$ $\rightarrow CH_3 + ?$		Kanofsky, *et al* (1972)
iso-$C_4H_8 + O \rightarrow$ products	1.6×10^{-11}	Elias (1963)
	$3.1 \times 10^{-11}\ e^{-200/T}$	Cadle and Allen (1971)
	$1.0 \times 10^{-11}\ e^{-0/T}$	Atkinson and Cvetanovic (1972)
	3.8×10^{-12}	Braun and Lenzi (1967)
cis-2-Pentane + O → products	1.8×10^{-11}	Ford and Endow (1957)

TABLE IV
cont'd

C. Ethylene and ethane

Reaction	Rate Constant	ΔH_{298}	Reference
$C_2H_4 + O \rightarrow CH_3 + CHO$	6.3×10^{-13}	-43.1	Stuhl and Niki (1971)
	5.2×10^{-13}		Niki, Daby and Weinstock (1967)
	6.25×10^{-13} (298°K)		Stuhl and Niki (1972b)
	Verification of Products (90%)		Kanofsky, et al (1972)
	$5.4 \times 10^{-12}\ e^{-570/T}$		Davis, et al (1972)
	$1.7 \times 10_{-11}\ e^{-800/T}$		Cadle and Allen (1971)
	1.2×10^{-12} (300°K)		Elias and Schiff (1960)
	Activ. Energy 0.60 to 1.0 Kcal		DeMore (1972)
$C_2H_4 + O \rightarrow H_2CO + CH_2$	? (small, see above)	-4.5 ± 4	Westenberg and deHaas (1969)
$C_2D_4 + O \rightarrow$ products	$\approx 5.6 \times 10^{-13}$ (298°K)		Stuhl and Niki (1972b)
$C_2H_4 + OH \rightarrow$	5×10^{-12} (= nk)*		Wilson and Westenberg (1967)

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* n is an unknown stoichiometric coefficient.

TABLE IV
cont'd

$C_2H_4 + OH \rightarrow$ products $(CH_3CHO) + H$	1.8×10^{-12}		Morris, *et al* (1971)
$C_2H_4 + H \rightarrow C_2H_5$	1.0×10^{-12}		Braun and Lenzi (1967)
	1.1×10^{-12}		Penzhorn and Darwent (1971)
	$1.31 \times 10^{-12}\ e^{-370/T}$		Teng and Jones (1972)
$C_2H_4 + HO_2 \rightarrow$ products	$1.7 \times 10^{-14}\ e^{-3500/T}$		Lloyd (1972)
$C_2D_4 + H \rightarrow C_2HD_4$	2×10^{-12}		Braun and Lenzi (1967)
$C_2H_6 + O \rightarrow C_2H_5 + OH$	$4.6 \times 10^{-11}\ e^{-3250/T}$		Papadopoulas, *et al* (1971)
	$6.6 \times 10^{-11}\ e^{-3300/T}$	-4.0	Herron and Huie (1969)
	$4.2 \times 10^{-11}\ e^{-3200/T}$		Recommended by Herron (1969)
$C_2H_6 + OH \rightarrow$ products	$\sim 1 \times 10^{-12}$		Wilson and Westenberg (1967)
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	3.3×10^{-13}		Papadopoulas, *et al*, (1971)
	2.9×10^{-13} (302°K)		Greiner (1967).
	$1.9 \times 10^{-11}\ e^{-1230/T}$		Greiner (1970a)
	$1.1 \times 10^{-10}\ e^{-1800/T}$		Wilson (1972) rec.
$C_2H_6 + H_2O \rightarrow$ products	4.7×10^{-23}		Baldwin, *et al* (1971)

TABLE IV
cont'd

D. Acetylene and Methylacetylene

Reaction	Rate Constant	ΔH_{298}	Reference
$C_2H_2 + O \rightarrow CH_2 + CO$	$4.3 \times 10^{-11}\ e^{-1600/T}$ (297-398°K)		Sanders and Heichelen (1966)
$C_2H_2 + O \rightarrow CH_2 + CO^{\dagger}$		-51	Liu, *et al* (1972)
		-48	Clough and Thrush (1968)
		-47	Lin (1972)
$C_2H_2 + O \rightarrow CH_2 + CO$	$2\text{-}3 \times 10^{-11}$ (1000-1600°K)		Fenimore and Jones (1963)
	1.5×10^{-13} (300°K)		Sullivan and Warneck (1965)
	1.8×10^{-13} (300°K)		Arrington, *et al* (1965; 1967)
	not the only reaction occurring		Williamson and Bayes (1969)
$C_2H_2 + O \rightarrow$ products	$1.31\ \ 10^{-13}$ (300°K)		Stuhl and Niki (1971)
$C_2H_2 + O \rightarrow CH_2 + CO$	$8.3 \times 10^{-11}\ e^{-1250/T}$		Browne, *et al* (1969)
$C_2H_2 + O \rightarrow CH_2 + CO$	$(2.4 \pm .8) \times 10^{-11}\ e^{-(1780 \pm 100)/T}$		James and Glass (1969)
$C_2H_2 + O \rightarrow HC_2O + H$		-23.3	Becker, *et al* (1969)
$C_2H_2 + O \rightarrow C_2O + H_2$		-22	Becker, *et al* (1969)

TABLE IV
cont'd

$C_2H_2 + O \rightarrow CH_2CO$	0.25		
$\rightarrow CH_2 + CO$	~0.15-.45	0.75 total	Jones and Bayes (1972)
$\rightarrow HCCO + H$	0.60-.30		
$\rightarrow CCO + H_2$	0.003		
$C_2H_2 + O \rightarrow CH_2\ ,\ C_2HO$			Kanofsky, <u>et</u> <u>al</u> (1972b)
$C_2H_2 + O \rightarrow CH_2 + CO$		42% by this channel	Williamson (1971)
$C_2H_2 + OH \rightarrow$ products		$\sim 1 \times 10^{-12}$	Wilson and Westenberg (1967)
$C_2H_2 + OH \rightarrow C_2H + H_2O$		$1 \times 10^{-11}\ e^{-3500/T}$	Browne, <u>et</u> <u>al</u> (1969)
$C_2H_2 + OH \rightarrow CO + CH_3$		product identification (CH_3 impurity in OH??)	Gehring, <u>et</u> <u>al</u> (1970)
$C_2H_2 + OH \rightarrow C_2H_2O + H$		product identification only product found	Kanofsky, <u>et</u> <u>al</u> (1972b)
$C_2H_2 + OH \rightarrow C_2H + H_2O$		$2.3 \times 10^{-11}\ e^{-3500/T}$	Fenimore and Jones (1964)
		2×10^{-13} (300-1000°K)	Wilson (1972) rec.
		$1 \times 10^{-11}\ e^{-3500/T}$ (1000-1600°K)	
$HCCCD_3 + O \xrightarrow{1.0 \pm .09} C_3D_3O + H$ $HCCCD_3 + O \xrightarrow{.1 \pm .06} C_3D_2HO + D$		product identification	Kanofsky, <u>et</u> <u>al</u> (1972b)
$DCCCH_3 \xrightarrow{1.0 \pm .15} C_3H_3O + D$ $DCCCH_3 \xrightarrow{.11 \pm .05} C_3H_2DO + H$		product identification	Kanofsky, <u>et</u> <u>al</u> (1972b)

TABLE IV
cont'd

$O + CD_3C\equiv CH \xrightarrow{1.0 \pm .18} CD_3 + HC_2O$ $\xrightarrow{.05 \pm .17} CD_2H + DC_2O$	product identification	Kanofsky, et al (1972b)
$O + CH_3C\equiv CH \rightarrow CO + CH_3CH \longleftrightarrow C_2H_4^*$ $\searrow \quad \swarrow$ $C_2H_2^* + H_2$		Kanofsky, et al (1972b)
$DC\equiv CCH_3 + O \xrightarrow{1.0 \pm .08} C_2H_3 + DCO$ $\xrightarrow{.25 \pm .06} C_2H_2D + HCO$	product identification	Kanofsky, et al (1972b)
$HC\equiv CCH_3 + O \rightarrow C_2H_2O + CH_2$	product identification	Kanofsky, et al (1972b)
$HC\equiv CCD_3 + OH \xrightarrow{1.0 \pm .18} CD_3 + C_2H_2O$ $\xrightarrow{.04 \pm .2} CD_2H + C_2HDO$ $\xrightarrow{.02 \pm .15} CH_2D + CD_2O$	product identification	Kanofsky, et al (1972b)
$HC\equiv CCH_3 + OH \rightarrow C_3H_4O + H$	product identification	Kanofsky, et al (1972b)
$HC\equiv CCH_3 + OH \xrightarrow{1.0} C_3H_2D + H_2O$ $\xrightarrow{.04 \pm .05} C_3H_3 + HDO$	product identification	Kanofsky, et al (1972b)

TABLE IV
cont'd

E. Carbonyl (-C = O)

Reaction	Rate Constant	ΔH_{298}	Reference
$HCO + HCO \rightarrow H_2CO + CO$		-48	Westenberg and DeHaas (1969)
$HCO + O \rightarrow CO_2 + H$		-99	Westenberg and DeHaas (1969)
$HCO + O \rightarrow CO + OH$	5×10^{-11} (EST)(1000-1700°K)		Browne, *et al* (1969)
		-79	Becker, *et al* (1969)
$HCO + O \begin{array}{l} \xrightarrow{k} CO + OH \\ \xrightarrow[k']{} H + CO_2 \end{array}$	$k'/k = 0.73 \pm 0.15$		Westenberg and DeHaas (1972)
	$k'/k = 0.25$		Niki, *et al* (1969)
		-84	Clough and Thrush (1968)
$HCO + O \rightarrow CO + OH^{\dagger}$	$> 8 \times 10^{-13}$		Malki (1972)
$HCO + H \rightarrow H_2 + CO$	3.3×10^{-11} (EST)(1000-1700°K)		Browne, *et al* (1969)
$HCO + OH \rightarrow H_2O + CO$	5×10^{-11}(EST)(1000-1700°K)		Browne, *et al* (1969)
$HCO + O_2 \rightarrow CO + HO_2$	$< 10^{-17}$	-18.88	McMillan and Calvert (1965)
	2×10^{-13}		Demerjian, Kerr, and Calvert (1972)

TABLE IV
cont'd

$HCHO + OH \rightarrow H_2O + CHO$	$> 6.7 \times 10^{-12}$		Herron and Penzhorn (1969)
	1×10^{-10}		Kondratiev, V. (1972)
	$8.3 \times 10^{-9 \pm 1}\ e^{-6500/T}$ (700-1000°K)		Wilson (1972) rec.
$HCHO + O \rightarrow CHO + OH$	1.5×10^{-13}	-26	Westenberg and DeHaas (1969)
	3.5×10^{-14} *		Cadle and Allen (1971); Niki (1966)
$HCHO + HO_2 \rightarrow H_2O_2 + HCO$	$8 \times 10^{-13}\ e^{-750/T}$		Lloyd (1972)
$HCHO + O_2 \rightarrow HCO + H_2O$	2×10^{-23} (440°C)		Baldwin, _et_ _al_ (1971)
$HCHO + H_2O \rightarrow CHO + H_2O_2$	2.3×10^{-15} (440°C)		Baldwin, _et_ _al_ (1971)**
$HCHO + H \rightarrow H_2 + HCO$	$6.3 \times 10^{-11}\ e^{-1890/T}$		Westenberg and DeHaas (1972b)
$CH_2CO + H \rightarrow HC_2O + H_2$		~0	Becker, _et_ _al_ (1969)
$C_2H_5CHO + O_2 \rightarrow C_2H_5CO + H_2O$	1.3×10^{-22} (440°C)		Baldwin, _et_ _al_ (1971)
$C_2H_5CHO + O_2 \rightarrow C_2H_5CO + H_2O_2$	3×10^{-15} (440°C)		Baldwin, _et_ _al_ (1971)

---

* $E < 5500$

** Assuming 3×10^{-12} for $2HO_2 \rightarrow H_2O_2 + O_2$.

TABLE IV

cont'd

$CH_3CHO + O \rightarrow CH_3CO + OH$	$1.8 \times 10^{-11}\ e^{-1150/T}$	Cadle and Allen (1971)
	4.5×10^{-13} (300°K)	Cadle and Powers (1967)
$CH_3CHO + O \rightarrow$ products	$7.9 \times 10^{-11}\ e^{-1500/T}$	Cadle and Allen (1971)
	5.3×10^{-13} (300°K)	Cvetanovic (1956)
$CH_3CO + OH \rightarrow CH_3CO + H_2O$		Cadle and Allen (1971)
$CH_3CHO + OH \rightarrow$ products (CH_3, CO, CH_2CO)	1.5×10^{-11}	Morris, *et al* (1971)
$CH_3CO + OH \rightarrow$ products	fast	Morris, *et al* (1971)
$CH_3 - CH_2CHO + O \rightarrow$ products	$1.3 \times 10^{-10}\ e^{-1900/T}$	Cadle and Allen (1971)

TABLE IV
cont'd

F. C Fragments and other C Compounds

Reaction	Rate Constant	ΔH_{298}	Reference
$C_2 + OH \rightarrow CH^* + CO$		-94	Williams and Smith (1969)
	8×10^{-11} at 2200°K		Bulewicz, et al
$C_2 + NO \rightarrow CN^* + CO$		-136	Williams and Smith (1969)
$C_2 + O \rightarrow C + CO$		-113	Williams and Smith (1969)
$C_2 + OH \rightarrow CH + CO$	8.3×10^{-12} (2200°K)		Wilson (1972) rec.
$C_2 + OH \rightarrow CH^* + CO$			Gaydon (1957) Peeters et al (1971)
$\rightarrow CH(^2\Delta)$	6×10^{-13}		Porter, et al (1967)
$\rightarrow CH(B^2\Sigma^-)$	7×10^{-14}		Porter, et al (1967)
		-91.7	Smith (1972)
$C_2O^\dagger + O \rightarrow CO(A^1\Pi) + CO(X^1\Sigma)$			Marmo, et al (1967)
$C_2O + O \rightarrow CO^* + CO$			Becker, et al (1969)
$\rightarrow CO(A^1\Pi, v \leq 6; e^3\Sigma^-, v \leq 6; d^3\Delta, v \leq 9)$		≤ -205	Smith (1972)
$\rightarrow CO(A^1\Pi, d^3\Delta, e^3\Sigma)$	VUV Quantum yield = $10^{-4.3 \pm 0.5}/C_2H_2$		Becker and Bayes (1968)

TABLE IV
cont'd

$C_2O + O \rightarrow$ all states	10^{-10}		Shackleford, *et al* (1972)
$\rightarrow CO(A^1\pi) + CO(X^1\Sigma)$	10^{-11} to 10^{-12}		
$CC^{16}O + {}^{18}O \rightarrow C^{18}O^* + C^{16}O^*$	Fourth positive observed for both systems		Bayes (1970)
$C_2O + OH \rightarrow CH^* + CO_2$		-54(?)	Williams and Smith (1970)
$C_2O + H \rightarrow CH + CO$		-29.5	Becker, *et al* (1969)
$C_2O + O_2 \rightarrow 2CO + O$	(560-680°C)		LeBel and Oullet (1971)
$C_2O + O_2 \rightarrow$ products	1.7×10^{-12} (all products)		Shackelford *et al* (1972)
$C_2O + NO \rightarrow$ products	1.2×10^{-10}		Shackleford *et al* (1972)
$HCCO + H \rightarrow C_2O + H_2$		~0	Becker, *et al* (1969)
$HCCO + O \rightarrow H + 2CO$	2×10^{-12}		Jones and Bayes (1972)
$HCCO + C_2H_2 \rightarrow$ products	$< 8 \times 10^{-16}$		Jones and Bayes (1972)
$C_2H_5 + O \rightarrow C_2H_4 + OH$		-65	Papadopoulas, *et al* (1971)
$\rightarrow C_2H_5O^*$		-92	

TABLE IV
cont'd

$C_2H_5 + H \rightarrow C_2H_6$ 1% (est)			Papadopoulas, et al (1971)
$\rightarrow 2CH_3$			
$\rightarrow C_2H_4 + H_2$			
$C_2H + O \rightarrow CH + CO$	1×10^{-10} (est)		Browne, et al (1969)
		-60.5	Smith (1972)
$C_2H^* + O \rightarrow CH(A^2\Delta) + CO$			Brennen and Carrington (1967)
$C_2H + O \rightarrow C_2^* + OH$	endothermic		Williams and Smith (1969)
$C_2H + O_2 \rightarrow HCO + CO$	$1.8 \times 10^{-11}\ e^{-3500/T}$ (est)		Browne, et al (1969)
$C_2H + H \rightarrow C_2^* + H_2$	endothermic		Williams and Smith (1969)
$C_3O_2 + O \rightarrow C_2O + CO_2$			LeBel and Ouellet (1971)
		~38	Becker, et al (1969)
$C_3O_2 + H \rightarrow HC_2O + CO$		-16.6	Becker, et al (1969)
$C + CH \rightarrow C_2^* + H$ (Swan)		-62	Williams and Smith (1970)

TABLE IV
cont'd

$CH + O_2 \rightarrow CO + OH(A^2\Sigma)$	1×10^{-13}		Porter, et al (1967)
		-158	Becker, et al (1969)
		-159.5	Smith (1972) Krishnamachari and Broida (1961)
$CH^{\dagger} + O_2 \rightarrow CO^* + OH$	not important in shocks		Homer and Kistiakowski (1966)
$CH^{\dagger} + O \rightarrow CO^* + H$	not important in shocks		Homer and Kistiakowski (1966)
$CH + CO(a^3\pi) \rightarrow CO(X) + CH(A^2\pi)$			Smith (1972)
$CH + NO \rightarrow NH^*(A^3\pi) + CO$		-109	Williams and Smith (1969)
$CH_2 + O \rightarrow HCO + H$	5×10^{-11}(est)		Browne, et al (1969)
$CH_2 + O \rightarrow CO + 2H$		-77	Westenberg and DeHaas (1969)
$CH_2 + O \rightarrow CO^{\dagger} + 2H$		-76.8	Clough and Thrush (1968)
		-71	Liu, et al (1972)
$CH_2 + O \rightarrow CO + 2H$	$>2.5 \times 10^{-12}$		Jones and Bayes (1972)
$CH_2^{\dagger} + O \rightarrow HCO^*(Vaidya) + H$			Williams and Smith (1969)
$CH_2 + OH \rightarrow HCO + H_2$	1×10^{-10}(est)		Browne, et al (1969)
$CH_2 + C \rightarrow C_2^* + H_2$		-67.7	Peeters, et al (1971)

TABLE IV
cont'd

$CH_2 + CH_2 \rightarrow CH + CH_3$		-11	Becker and Kley (1969)
$CH_2 + C_2H_2 \rightarrow C_3H_4$	$> 1 \times 10^{-12}$		Jones and Bayes (1972)
$CH_2 + O_2 \rightarrow CHO + OH$		-89±10	Williams and Smith (1970)
$CH_2 + O_2 \rightarrow$ products	$< 10^{-15}$ (300°K)		Shackleford and Mastrup (1973)
$CH_3 + CHO \rightarrow CH_3CHO$	6.3×10^{-12}		Quee and Thynne (1968)
$CH_3 + CHO \rightarrow CH_4 + CO$	3.7×10^{-11}		Quee and Thynne (1968)
$CH_3 + OH \rightarrow$	6.7×10^{-12}		Wilson (1972) rec.
$\rightarrow CH_4 + O$	$\sim 7 \times 10^{-12}$ (1970-2190°K)		Fenimore (1968)
$CH_3 + O \rightarrow CH + H_2O$		-8	Becker and Kley (1969)
$CH_3 + O \rightarrow H_2CO + H$	$\geq 3 \times 10^{-11}$	-67	Niki, Daby, and Weinstock (1969)
	3.2×10^{-11} (1200-1900°K)		Fenimore and Jones (1961)
$CH_3 + O \rightarrow CHO + H_2$			Jones and Bayes (1971)
$CH_3 + H \rightarrow CH_4$	$1.95 \times 10^{-12}\ e^{-25/T}$		Teng and Jones (1972)
$CH_3 + CH_3 \rightarrow C_2H_6$	$4.36 \times 10^{-11}\ e^{-220/T}$		Teng and Jones (1972)
$CH_3 + C_2H_5 \rightarrow C_3H_8$	$4.17 \times 10^{-11}\ e^{-200/T}$		Teng and Jones (1972)
$CH_3 + O_2 \rightarrow CH_2O + OH$		-53	McMillan and Calvert (1965)

TABLE IV
cont'd

$CH_3OH + O \rightarrow HCHO + H_2O$	$8.5 \times 10^{-13}\ e^{-1560/T}$ (347-400°K)		Avramenko, *et al* (1961)
$CH_4 + O \rightarrow CH_3 + OH$	1.4×10^{-16} (300°K)		Cadle and Allen (1971)
	$3.6 \times 10^{-11}\ e^{-4460/T}$	-.44	Herron and Huie (1969)
	$3.5 \times 10^{-11}\ e^{-4550/T}$		Recommended by Herron (1969)
$CH_4 + OH \rightarrow CH_3 + H_2O$	$4.7 \times 10^{-11}\ e^{-2500/T}$	-17.3	Wilson (1972) rec.
	$4.8 \times 10^{-11}\ e^{-2500/T}$		Wilson and Westenberg (1967)
	$5.5 \times 10^{-12}\ e^{-1900/T}$		Greiner (1970a)
	5×10^{-12} (at 1285°K)		Dixon-Lewis and Williams (1967)
	$4.2 \times 10^{-11}\ e^{-2550/T}$		Dixon-Lewis and Williams (1967)
	$4.1 \times 10^{-11}\ e^{-2500/T}$		Baker, *et al* (1971)
	$6 \times 10^{-10}\ e^{-4500/T}$ (950-1500°K)		Fenimore and Jones (1961)
	$4 \times 10^{-10}\ e^{-3570/T}$ (950-1500°K)		Baldwin, *et al* (1967)
$CH_4 + H \rightarrow CH_3 + H_2$	6.7×10^{-14} (at 900°K)	-2.3	Dixon-Lewis and Williams (1967)
	$1 \times 10^{-10}\ e^{-6300/T}$		
$CH_4 + H \rightarrow CH_3 + H_2$	$2.5 \times 10^{-10}\ e^{-7400/T}$		Thrush (1965)

TABLE IV
cont'd

$CH_4 + H \rightarrow CH_3 + H_2$	$1.2 \times 10^{-10}\ e^{-5900/T}$		Kurylo and Timmons (1969)
	$2 \times 10^{-10}\ e^{-5950/T}$		Baker, et al (1971)
	$3 \times 10^{-10}\ e^{-6300/T}$		Baldwin, et al (1967)
$CO + OH \rightarrow CO_2 + H$	$5.2 \times 10^{-13}\ e^{-300/T}$	25	Wilson (1972) rec.
$CO + OH \rightarrow CO_2 + H$	$k = CQ(T)^*$		Dryer, et al (1971)
$CO + H_2O \rightarrow CO_2 + H$	10^{-12} (300°K)		Est. by Westenberg (1972)
	$< 10^{-19}$ (300°K)		Est. by Doug Davis (1972)
	$\sim 10^{-15}$		Est. by Stuhl and Niki (1972)

$$* \quad Q(T) = \frac{300}{T} \; \frac{\left[1 - e^{-5370/T}\right]\left[1 - e^{-3125/T}\right]}{\left[1 - e^{-2400/T}\right]\left[1 - e^{-1899/T}\right]\left[1 - e^{-1188/T}\right]\left[1 - e^{-876/T}\right]\left[1 - e^{-852/T}\right]}$$

$C = 1.25 \times 10^{-13}$ (Dryer, et al); Recommend $2 \times 10^{-13} = C$

TABLE IV
cont'd

G. Reactions of Hydrogen and Oxygen

Reaction	Rate Constant	ΔH_{298}	Reference
$H + O_2 + M \rightarrow HO_2 + M$	$2.4 \times 10^{-32}\ e^{238/T}$		Huie and Davis (1972)
$M = N_2$			
(Temp. dep. from $M = He$)			
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.3×10^{-12} (300°K)		
	$1.7 \times 10^{-11}\ e^{-500/T}$	-42.6 ± 4	NBS CIAP Eval.
$O + HO_2 \rightarrow OH + O_2$	$8 \times 10^{-11}\ e^{-500/T}$		Lloyd (1972)
$H + O_3 \rightarrow 2\,OH$	2.6×10^{-11}	-76.9	NBS CIAP
$H + O \rightarrow OH(A^2\Sigma)$	3×10^{-21}		Ticktin, *et al* (1967)
	$< 10^{-23}$		Schiff, priv. comm. (1973)
$H + HO_2 \rightarrow OH^\dagger + OH$	$1.7 \times 10^{-10}\ e^{-900/T}$	-39	Charters and Polanyi (1960)
$HO_2 + OH \rightarrow H_2O + O_2$	$1.7 \times 10^{-11}\ e^{-500/T}$		Lloyd (1972)
$OH + OH \rightarrow H_2O + O$	8.4×10^{-13}		Breen and Glass (1970)
$OH + H_2 \rightarrow H_2O + O$	2.6×10^{-12} (300°K)	$-17.$	Wilson (1972) rec.
$OH + O \rightarrow O_2 + H$	4.3×10^{-11}		Breen and Glass (1970)
	4.2×10^{-11}		Wilson (1972) rec.
$OH \xrightarrow{\text{wall}}$ orthoboric acid	124		Breen and Glass (1970)

TABLE IV
cont'd

$OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-11} e^{-1800/T}$ $(1.2 \pm .3) \times 10^{-12}$ (298°K)		Wilson (1972) rec. Gorse and Volman (1972)
$OH + H \rightarrow H_2 + O$	$2.2 \times 10^{-11} e^{-4000/T}$ (500-3000°K)		Wilson (1972) rec.
$OH + H_2 \rightarrow H_2O + H$	$3.8 \times 10^{-11} e^{-2600/T}$	-15.1	Wilson (1972) rec.

Reactions of Oxygen

$O + O_2 + M \rightarrow O_3 + M$	$6.6 \times 10^{-35} e^{511/T}$	-25.4	Huie and Davis (1972)
$O + O_3 \rightarrow 2O_2$	$2.0 \times 10^{-11} e^{-2410/T}$	-93.6	NBS CIAP Eval.

APPENDIX II

STANDARD HEATS OF FORMATION, ΔH^{f}_{298}, kcal/gmole

H	52.1
O	59.56
OH	9.33
HO_2	4.96
H_2O	-57.80
H_2O_2	-31.83 to -32.6
CH	141.0
CH_2	92 to 95.0
CH_3	31.9 to 34
CH_4	-17.90
C	170.89
C_2	199.0 ± 2
C_2H_6	-20.24
C_3H_8	-24.82
$n\text{-}C_4H_{10}$	-30.15
$n\text{-}C_5H_{12}$	-35.00
$n\text{-}C_6H_{14}$	-39.96
C_2H_2	54.19
C_2H_4	12.50
C_3H_6	4.88
C_4H_8	- .03
C_5H_{10}	-5.00
C_6H_{12}	-9.96

CO	-26.42
CO_2	-94.05
CHO	7.2 to 11.0
HCHO	-27.7
C_2O	68 to 92*
C_2H	117 to 122
H_2C_2O	-14.5
HC_2O	38.4
C_2H_3	69 ± 2
C_2H_5	26.0
$n\text{-}C_3H_7$	21.0
$i\text{-}C_3H_7$	17.6
$i\text{-}C_4H_9$	13.7
$t\text{-}C_4H_9$	6.7
$CH_3O\cdot$	3.5
$CH_3 - CHO$	-39.76
CH_3CO	-5.4
CN	111.
N	112.965

* Spectroscopic constants given by Devillers and Ramsay (1971)

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APPENDIX III

HYPOTHESIZED COMPOSITION (40% BY WEIGHT OF TURBINE FLOW) OF ATLAS TURBINE GAS HYDROCARBON SPECIES

Species	Mass Fraction
"A" *	.60
"O" **	.20
C_2H_6	.05
C_2H_4	.05
CH_4	.05
CH_2O	.05
all radicals	0

* refers to a saturated hydrocarbon, C_nH_{2n+2} with $n \geq 3$

** refers to an olefinic hydrocarbon, C_nH_{2n} with $n \geq 3$

These mole fractions have been used in initial examinations of the role of IR Chemiluminescence in the Atlas sustainer plume.

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APPENDIX IV

A COMPARISON OF EXPERIMENTAL DATA FOR O AND OH + HC vs THE CHOICE OF LUMPED PARAMETER RATE CONSTANTS

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FIGURE 5.

Illustration of experimental data for hydrocarbon plus oxygen atom reaction rate constants compared with the choice of the lumped parameter rate constants for oxygen atom attack. The solid lines refer to experimental observations, believed to be accurate to ± 20% from 1000°K to 250°K, while the dotted lines refer to the lumped parameter choice herein. (n5 = normal pentane and 1-3 = 1-propylene).

Alkane data was taken from the extensive data of Herron and Huie (1969). Olefinic data was taken from Atkinson and Cvetanovic (1972). Other values for higher olefins are $\geq 10^{-11}$ at room temperatures as shown by the shaded block, (see Table IV for more detail) which led to the choice of 10^{-11} for the lumped parameter rate constant for $Ol + O \rightarrow R + CHO$. Assuming that the fuel will consist mainly of hydrocarbons greater than C5, we have recommended a conservative rate constant for the rate controlling step, $A + O \rightarrow R + OH$. Note that C_2H_6 is considered as a separate species.

FIGURE 5

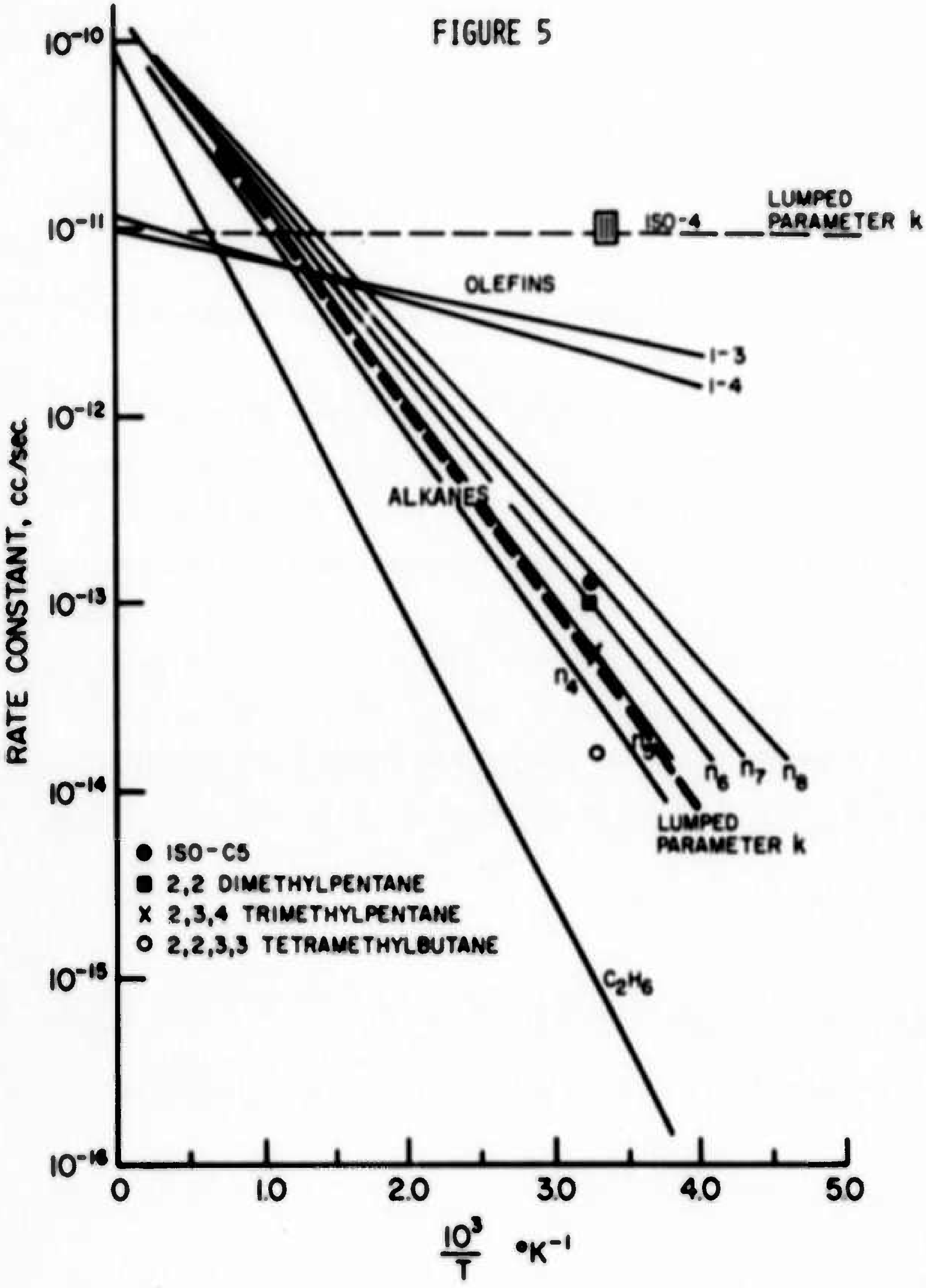
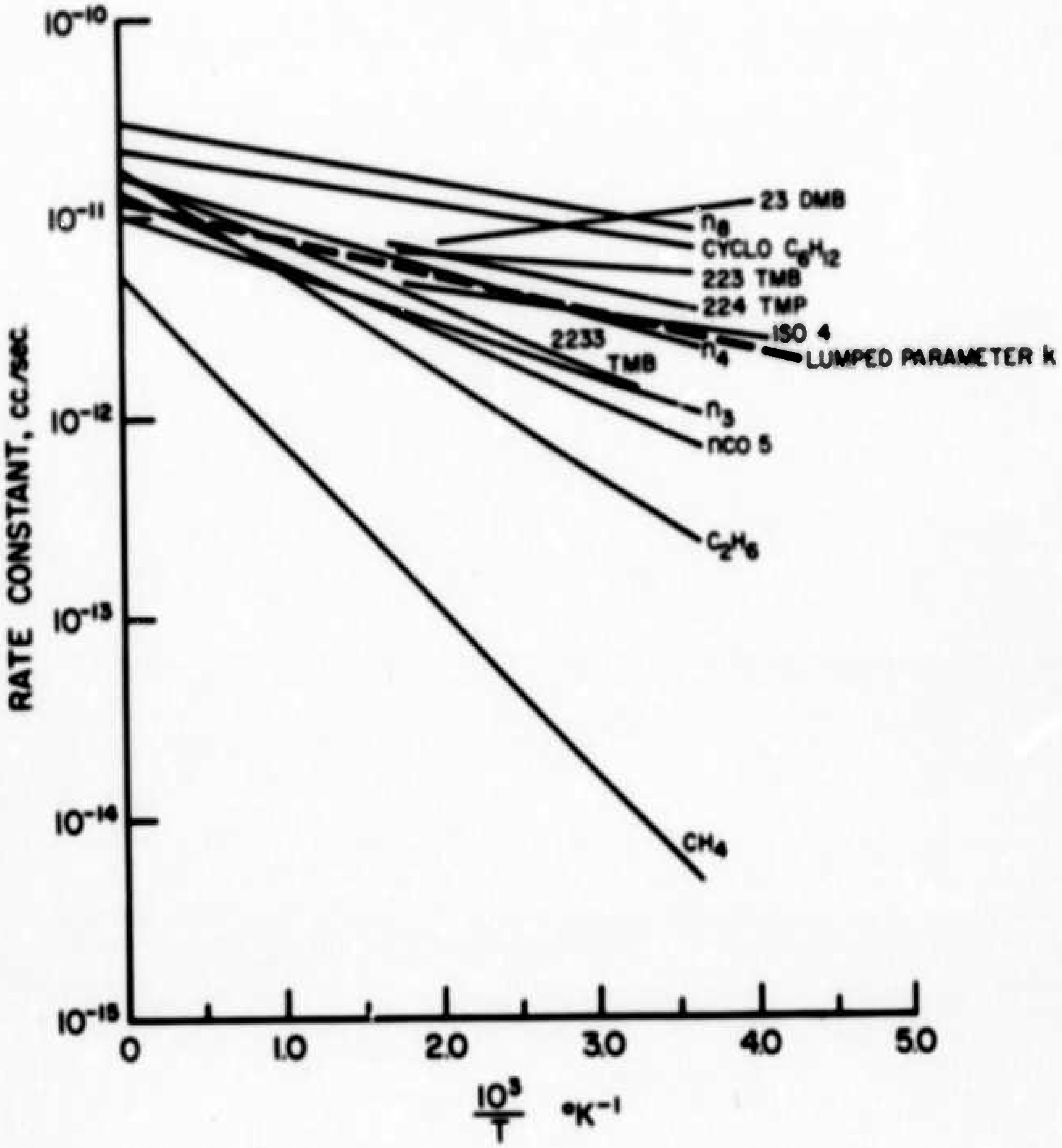

RATE CONSTANT, cc/sec
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
0
1.0
2.0
3.0
4.0
5.0
$\frac{10^3}{T}$ °K^{-1}
LUMPED PARAMETER k
ISO-4
OLEFINS
1-3
1-4
ALKANES
n_4
n_5
n_6
n_7
n_8
LUMPED PARAMETER k
C_2H_6
● ISO-C5
■ 2,2 DIMETHYLPENTANE
X 2,3,4 TRIMETHYLPENTANE
O 2,2,3,3 TETRAMETHYLBUTANE

FIGURE 6.

Illustration of experimental data for OH reaction rate constants with saturated hydrocarbons compared with the choice of the lumped parameter rate constant. The solid lines are the data of Greiner (1970) with an average uncertainty of ± 30% expected over the range of temperatures illustrated. As before C_2H_6 is treated separately in the proposed model. CH_4 is also treated separately. Thus, over the entire range of plume temperatures it is anticipated that the chosen lumped parameter rate constant for $A + OH \rightarrow R + H_2O$ should be accurate to within a factor of three regardless of the distribution of alkanes.

FIGURE 6



10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
RATE CONSTANT, cc./SEC
23 DMB
n_8
CYCLO C_6H_{12}
223 TMB
224 TMP
ISO 4
n_4
LUMPED PARAMETER k
2233 TMB
n_3
nco 5
C_2H_6
CH_4
0
1.0
2.0
3.0
4.0
5.0
$\frac{10^3}{T}$ °K^{-1}

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