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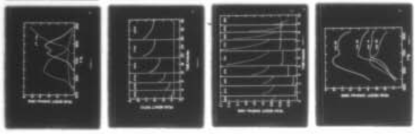

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The Decomposition of Ethanol, Propanol and Acetic Acid Chemisorbed on Magnesium Oxide

by

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and J. M. White

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The Decomposition of Ethanol, Propanol and Acetic Acid Chemisorbed on Magnesium Oxide*

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Abstract

Adsorption of ethanol, propanol, or acetic acid at 10^{-5} torr for 10 minutes on magnesium oxide powder, followed by evacuation for 20 minutes and then temperature programmed thermal desorption at a rate of 150 K min^{-1}, yielded the dehydration products ethylene, propylene, and ketene, respectively, while the dehydrogenation products were below detection limits. Several experiments with ethanol chemisorbed on magnesium oxide doped with various transition metals revealed that such impurities have the effect of lowering the temperature at which ethylene is desorbed. A mechanism is proposed which accounts for dehydration under low pressure conditions and dehydrogenation under high pressure conditions.

I. Introduction

The interaction of alcohols with magnesium oxide has been widely explored [1-7]. Generally, this catalyst has been found to be very selective towards dehydrogenation [2,6,7] in the presence of a relatively high pressure of adsorbate. Under such conditions, interactions are not limited to those between an adsorbed molecule and the surface, but may also include interactions between adsorbed species and the gas phase. For example, a recent IR study [1] of the adsorption of methanol on magnesium oxide indicates that two methoxide species are formed upon adsorption at room temperature. One desorbs as methanol between 400 and 600 K while the other is stable to temperatures above 600 K. Therefore, under typical dehydrogenation conditions of T ~ 600 K and high alcohol pressure, the gas phase alcohol would encounter predominately chemisorbed methoxide species. Another IR study of ethanol dehydrogenation on magnesia [2] noted that acetaldehyde was only produced in the presence of gas phase ethanol. When the flow of ethanol over the catalyst at 637 K was stopped, the production of acetaldehyde abruptly halted and a small amount of butadiene appeared. Most of the chemisorbed species (~75% acetate and 25% ethoxide) did not desorb, however.

Selectivity for dehydrogenation appears to be an anomalous property of magnesia [8]. Generally, metal oxides are predominately dehydrogenating when the metal ion can readily change its valence state, whereas oxides in which the metal ion has its outermost occupied orbitals completely filled are usually predominately dehydrating. Clearly, magnesia is an exception to this generality.

The following properties of magnesia have been noted by Linsen [7]: (1) The overall activity of magnesia is very low as compared to other dehydrogenating catalysts. (2) A copper catalyst at 413 K has a dehydrogenating activity comparable to a magnesia catalyst at 623 K. According to measured activation energies, when both catalysts are maintained at 413 K, the activity of magnesia is a factor of 10^7 lower than the copper catalyst. (3) The dehydration activity of alumina is more than a factor of 10^3 greater than that of magnesia. On the basis of these properties, Linsen [7] concluded that the selective character of magnesia for dehydrogenation arises because the dehydration reaction occurs with extremely low probability and makes it experimentally possible to detect a low activity for dehydrogenation. He suggested that the relatively basic character of the magnesia surface was responsible.

In the present study, which is part of a continuing effort in our laboratory to study alcohol reactions on various metal oxides [4,9], ethanol was adsorbed on magnesium oxide under low pressure (10^{-5} torr) conditions in order to minimize the interaction of the chemisorbed species with the alcohol vapor. After evacuation the chemisorbed species were thermally decomposed into a continuously pumped vacuum system at pressures in the low 10^{-7} torr range, again minimizing the interaction between gas phase and chemisorbed species. This procedure was followed for high purity MgO and for MgO intentionally contaminated with transition metal ions. Further information on the nature of the adsorbed species could be obtained through electron spectroscopic studies over a wide range of temperatures; this is currently being pursued in our laboratory.

II. Experimental

The catalyst was placed in a bakeable, ultra-high vacuum system with a background pressure of 5×10^{-9} torr. It was equipped with an ion pump, ionization pressure gauge, mass spectrometer, and two sample holders. The sample holders consisted of resistively heated V-shaped tantalum boats (similar in design to that shown in ref. [9], but without the screen). One holder contained the sample of interest while the other served as a reference. Temperatures were measured with a chromel-alumel thermocouple. An optical pyrometer was used to check the uniformity with which the boat heated; a thermal gradient of 40 K at 1073 K was found.

The catalyst [11] ($32.4\ m^2 gm^{-1}$) used in this study was prepared by precipitating the carbonate from a magnesium nitrate solution. The carbonate was then dried and heated in air at 1100 K for 4 hrs. 40 min. [10]. Approximately 1.5 mg of catalyst was placed in the sample holder, sealed in the vacuum chamber, and outgassed by heating to 1070 K. Typically, outgassing involved desorption of large amounts of H_2O, CO, and CO_2 between 670 K and 870 K.

Prior to every adsorption experiment, the substrate temperature was raised to 1070 K and held there until the pressure fell into the mid-10^{-8} torr range. This generally required only a few minutes and insured that gases adsorbed from the residual gas background (particularly water) were removed.

After cooling to less than 350 K (which required ~10 minutes), the ionization gauge and mass spectrometer filaments were turned off to avoid decomposition of the adsorbate. The adsorbate was then admitted by means of a variable leak valve while the system was continuously pumped. The ion pump current, which had been previously calibrated against the ionization gauge, served to measure the pressure of the adsorbate. All exposures were made at 10^{-5} torr for 10 minutes, followed by an evacuation period of 20 min. In order to outgas it, the mass spectrometer filament was turned on for the last 15 minutes of this evacuation period. Finally, the sample temperature was raised linearly at a typical rate of 150 K min^{-1} up to 1100 K. The output of the mass spectrometer (which repetitively scanned over some small mass range) and the sample temperature were recorded on a dual trace strip chart recorder.

The experimental results were found to be insensitive to the exposure and evacuation times. The same amount of desorbed material was obtained for exposure times of 5-20 minutes or evacuation times of 15-60 minutes.

III. Results

III.1. Pure MgO

The thermal decomposition of chemisorbed ethanol yielded ethylene and water at high temperatures, and a small amount of ethanol at low temperatures (fig. 1). No acetaldehyde or butadiene was observed in the thermal desorption spectra; however, according to Takezawa [2], the amount to be expected under our reaction conditions was much below our detection limits of ~1% of the total of all desorbed products. The temperature of maximum ethylene production was 990 K, while the water peak was extremely broad and appeared to increase until the maximum temperature was reached.

III.2. Effect of added cations

When these experiments were first begun, a stainless steel sample holder was used and a sharp ethylene desorption peak appeared at 570 K as shown in figure 2. Because this desorption temperature seemed too low in comparison to other work [2,15] and because of the possibility of contamination by the stainless steel, a tantalum sample holder was tested. When compared with Fig. 1, the results suggest that the magnesia was indeed contaminated with some species contained in the stainless steel. To investigate the effect of transition metal impurities on the decomposition of chemisorbed ethanol, the magnesium oxide powder was physically mixed with various transition metal oxides and outgassed in the vacuum chamber at 1100 K. This is a crude method of doping, in that the surface concentration of the transition metal cannot be controlled. Although more careful experiments are planned, the present results are nonetheless interesting and suggestive.

In one experiment a sample of NiO was placed in the blank sample holder in order to test for background effects, while a mixture of MgO(90%) and NiO (10%) was placed in the other holder. The NiO alone apparently did not adsorb ethanol; nothing appeared in the thermal desorption spectrum. One mixture evolved ethylene at 790 K with a second peak at 880 K (figure 3), while another such mixture evolved ethylene only at 570 K. The reason for such variations is not known but may be due to variations in the effective surface concentration of Ni^{2+}.

The same procedure was followed using Cu_2O, Fe_2O_3, and CoO. The Cu_2O alone evolved only acetaldehyde, but in very small quantity, due either to a low surface area or a reduction of the oxide. A mixture of Cu_2O and MgO evolved only ethylene and peaked at 770 K. Ferric oxide alone evolved large amounts of acetaldehyde, the peak temperature varying according to the time and temperature at which the sample was baked out. Generally it was lower for higher temperature treatments, and can probably be correlated with oxygen loss from the sample. The mixture with MgO evolved acetaldehyde and ethylene, with peak ethylene desorption at 770 K. A mixture of CoO and MgO evolved ethylene at 720 K while CoO, like NiO, desorbed nothing.

These qualitative results suggest that the presence of transition metals lowers the ethylene desorption temperature. This effect probably depends not only on the type of metal used, but also on its surface and bulk concentration and its oxidation state.

III.3. Steady-state production of ethylene

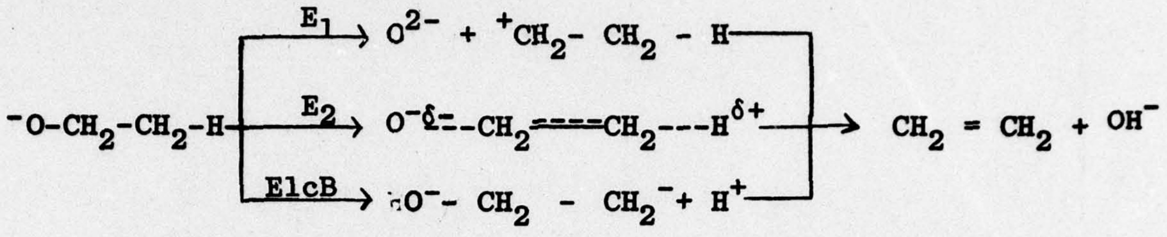
Figure 4 shows that under low pressure and high temperature conditions magnesium oxide can selectively dehydrate ethanol in a steady state situation. Ethanol was leaked into the system at a constant rate with an initial pressure of 5 x 10^{-7} torr. The catalyst was doped with NiO and was identical to that used for the experiment shown in Fig. 3. At the same temperature that ethylene begins to desorb in the thermal desorption experiments, the partial pressure of ethanol decreases slightly while the partial pressures of ethylene and water increase. No acetaldehyde was observed in this experiment; however, by extrapolating the results of previous studies [2] the amount expected would be much below our detection limit of ~2% of the partial pressure of ethanol. The experiment was repeated except the sample was predosed for 10 min. at room temperature with 10^{-5} torr of perdeuterated ethanol. After evacuation, ordinary ethanol was leaked in continuously at 5 x 10^{-7} torr while the catalyst temperature was varied. The results, shown in figure 5, allow one to distinguish the ethylene produced by decomposition of pre-adsorbed species from that produced in the steady state reaction. An increase in temperature results in the desorption of some C_2D_4 (dashed curve) and an increase in the partial pressure of C_2H_4. This continued with each temperature increase until most of the C_2D_4 was desorbed (873 K); further increases had little effect on the C_2H_4 pressure. Thus, it appears that the increase of the ethylene production rate with temperature is mostly due to an increased number of active sites, rather than increased activity of the available sites. These results are an indication of the intrinsic heterogeneity of the magnesium oxide surface which has been noted previously in methanol decomposition experiments [4]. The slow decline in activity after each temperature increase is also understandable in these terms (Fig. 4).

The thermal desorption results in figure 3 show that ethylene and water do not desorb simultaneously. Therefore, the desorption of water (which occurs at a higher temperature than the desorption of ethylene) should become the rate limiting step at some pressure of ethanol and would limit the dehydration activity at high alcohol pressures.

IV. The dehydration mechanism

In the following paragraphs mechanisms are proposed to account for the fact that magnesium oxide functions as a dehydration catalyst at very low ethanol pressures and as a dehydrogenation catalyst at relatively high ethanol pressures.

Three acid-base catalyzed reaction mechanisms can be distinguished for the dehydration of an aliphatic alcohol [12]. Assuming as discussed below, that ethoxide is formed by chemisorption of ethanol on magnesia, these three paths may be illustrated for ethoxide as:



For a dehydration to proceed by an El mechanism, there must be a strong acid present which interacts with the ethoxide oxygen. The acid behaves as a strong electron withdrawing group; it will decrease the electron density of the C-H and C-O bonds through an inductive effect. This decrease in electron density of the C-H bonds makes the hydrogens more acidic, so that as the C-O bond lengthens, the hydrogens become increasingly acidic and more prone to attack by the conjugate base of the acid that originally attacked the ethoxide oxygen. In a strict El elimination, the C-O bond becomes completely broken before a hydrogen is attacked by the base.

If the acid is not strong enough to break the C-O bond, then the reaction may require the cooperation of the base in order to proceed. In a strict E2 elimination, the C-O and C-H bonds are broken simultaneously.

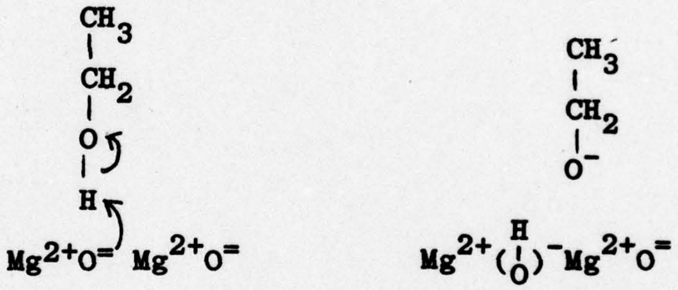
An ElcB mechanism, in which a strong base initiates the reaction by first abstracting a methyl hydrogen, is seldom observed for alcohols in solution. In solution, a strong base will preferentially attack the most acidic hydrogen, the hydroxyl hydrogen. The resulting negatively charged oxygen will function as a powerful electron releasing group which decreases the acidity of the methyl hydrogens. Then, for the dehydration to proceed, the base must attack one of these weakly acidic hydrogens and form the following species:

$$^{-}CH_2\text{-}CH_2\text{-}O^{-}$$

which must then lose an O^{2-} ion to form the olefin. Although this mechanism is highly unlikely in solution, it cannot be ruled out as the mechanism for ethylene formation on magensium oxide.

Owing to the electronegative natures of magnesium and oxygen, the magnesium oxide surface can be characterized by strongly basic oxygen ions and weakly acidic magnesium ions. A recent IR study [13] of the adsorption of NH_3 on a dehydrated magnesium oxide surface showed no evidence of Lewis acid sites; NH_3 adsorption occurs through hydrogen bonding to surface oxide ions rather than through nitrogen lone pair bonding to magnesium ions. Indeed, even in alumina, which has stonger Lewis acid sites than magnesia, the oxide ions are the active agents for olefin formation from alcohols [14]. This was shown by noting the effect that various poisons had on the activity for olefin formation. For example, pyridine, a strong Lewis base, coordinates with the aluminum ions and has no effect on olefin formation. However, tetracyanoethylene, which coordinates with the oxide ions, causes a considerable inhibition of activity for both olefin and ether formation.

Infra-red studies have generally shown that when an alcohol is adsorbed on magnesium oxide, surface alkoxide and hydroxyl species are formed. The formation of the ethoxide most probably occurs in a reaction between the strongest acids and bases present, which happen to be the hydrogen of the alcohol hydroxyl group and the surface oxide ions. If the oxide ion is more basic than the incipient alkoxide ion, then the hydrogen will be transferred from the alcohol to the oxide ion. The alkoxide then becomes associated with a magnesium ion largely for electrostatic reasons; the magnesium-alkoxide bond should be even more ionic than the Mg-O bond. The first step of the reaction should be (illustrated for ethanol):



As noted above, the preponderance of organic elimination reactions are best described in terms of the E2 rather than the ElcB pathway. In fact, it seems almost impossible to unequivocally establish the ElcB pathway. In the case of chemisorbed 2-hexanol and cis-2-methyl cyclohexanol decomposition on magnesia, the ElcB mechanism has been proposed but even here the evidence is not unequivocal [15].

One might argue that the ionic character of the ethoxide-magnesia interaction would make the alkoxide hydrogens less acidic than in the parent ethanol because, as the alcohol hydroxyl is deprotonated, the negative charge is released throughout the ethoxide. Subsequent ethoxide deprotonation by O^{2-} would occur on the β carbon but would require considerable activation energy thus accounting for the relatively high temperature required for ethylene production. In such a picture the absence of acetaldehyde production could be accounted for on the basis that there is no acid present which is strong enough to abstract a hydride from the α-carbon. Some support for these ideas comes from IR experiments which establish a correlation between the electro-negativity of the surface metal ion and the frequency of the CH vibration of the methyl group in the ethoxide [3,5]; the C-H stretching frequency increases with electronegativity.

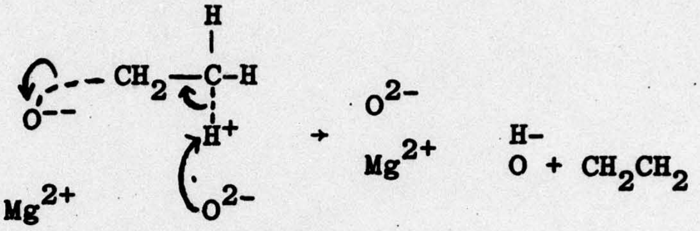
A very strong base is required if ethylene is formed by a strict ElcB mechanism. This base must deprotonate the ethoxide at the methyl site and leave a carbanion which decomposes to give ethylene. Some support for this view comes from a separate experiment in which perdeuterated ethanol was adsorbed in the presence of a small amount of H_2O. The resulting ethylene contained some hydrogen indicating that C-D bonds were broken and C-H bonds formed prior to cleavage of the C-O bond. If this exchange occurred at the methyl carbon then a carbanion intermediate and the ElcB path is indicated. However, we cannot clearly establish the site of exchange in our experiments. Perhaps the use of CD_3CH_2OD as an adsorbate would prove helpful but even if $CHDCH_2$ were found in the products the ElcB path would not be unequivocally established. Other evidence tends to support a mechanism which is more nearly E2 than ElcB. For example, in ammonia chemisorption [13] there are not IR bands reported which might be assigned to NH_2^-. On this basis deprotonation of ethoxide is not expected since it is a weaker acid than ammonia. Care must be exercised here, however, because ammonia deprotonation may require a large activation energy and the parent ammonia may desorb before such an energy requirement can be met thermally.

Another piece of evidence involves substitution of a methyl group for one of the β-hydrogens. In a separate series of experiments we compared the behavior of ethanol and 1-propanol. Adsorption of 1-propanol gave propylene which peaked about 30 K higher than the ethylene which desorbed after ethanol desorption. This shift was independent of heating rate over the range 75-150 K sec^{-1}. Substitution of the electron-releasing methyl group for a hydrogen will make the β hydrogens less acidic and should increase the energy requirement for the reaction as observed. This might be taken as support for the ElcB process, but because steric effects tend to operate in the same direction the evidence is not convincing.

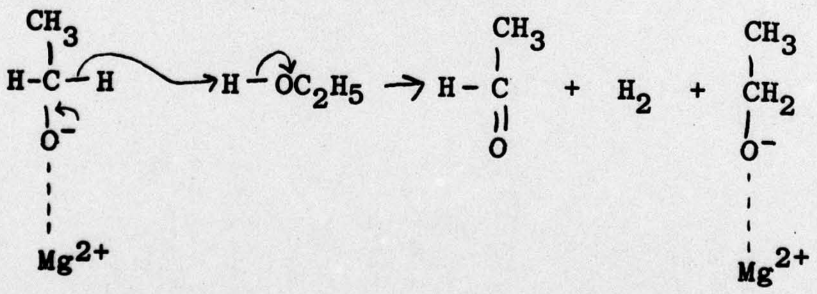
Some IR studies [2] have shown that under certain conditions alcohols can form adsorbed carboxylate species on magnesium oxide. In order to determine if acetate was an intermediate in the formation of ethylene, acetic acid (which adsorbs as acetate [2]) was used in place of ethanol. The thermal desorption spectrum (figure 6) shows that acetate itself was dehydrated to yield ketene and water. Since no ethylene was produced, it was concluded that under our experimental conditions ethoxide does not oxidize to acetate.

Since the evidence is inadequate to establish the ElcB pathway and since the bulk of organic elimination reactions do not follow this pathway, we have chosen to describe the present results using the E2 mechanism. In passing it should be noted that the E2 mechanism contains ElcB as one limit.

Along an E2 path, the decomposition would be represented as:



Gas phase (or physisorbed) alcohol molecules can behave as Bronsted acids. Recalling that the hydrogens on the α carbon are the easiest to abstract as H^- (due to the electron releasing properties of the alkoxide O^-), the following mechanism for acetaldehyde formation is possible:



These proposed mechanistic features suggest that the high selectivity for dehydrogenation at high alcohol pressures and the high temperature required for alcohol dehydration result from the low electronegativity of magnesium. We must now examine possible roles which added transition metal ions may play. The high temperature outgassing of the physical mixtures apparently gives rise to a small amount of cation exchange leading, in the case of MgO/NiO, to the presence of Ni^{2+} at the surface of the magnesia. Upon exposure to ethanol, ethoxide will be formed because the basic character of the surface oxide ions has not been lost, and these ethoxides may become associated with Ni^{2+} which has a higher electronegativity that Ng^{2+}. The higher electronegativity suggests that the ethoxide on the Ni^{2+} will carry less charge and all of its hydrogens will be more acidic than those of the ethoxide on the Mg^{2+}. Because of their greater acidity, the activation energy for abstracting an α hydrogen as H^- is raised, while the energy required to abstract a β hydrogen as H^+ is lowered. Thus, for a given temperature, the ethoxide associated with the Ni^{2+} should be more active for dehydration and less active for dehydrogenation, assuming that the surface oxide ions in both cases are of nearly equal basicity. This should be a good approximation as long as the Ni^{2+} concentration is low.

It has been observed by other workers that if one contaminates dehydration-dehydrogenation catalysts with alkali metal ions (less electronegative than the original metal), then the dehydration reaction is poisoned whereas the dehydrogenation reaction is unchanged [16].

V. Conclusion

Under conditions where the interaction between chemisorbed ethoxide and ethanol vapor is minimized, magnesium oxide functions as a highly selective dehydration catalyst, with a high activation energy for dehydration. Dehydration probably occurs through a typical acid-base catalyzed mechanism of roughly E2 type. Transition metals serve to lower the activation energy for dehydration, presumably by accepting some of the charge from the ethoxide ion, which increases the acidity of the β-hydrogens and makes the incipient oxide ion a better leaving group. The proposed mechanism also indicates that the surface ethoxide species can be dehydrogenated in the presence of a suitable gas phase Bronsted acid.

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Figure Captions

Figure 1. Thermal desorption spectrum of ethanol on pure MgO. — — — m/e 31 (ethanol); ------ m/e 18 (water); —— m/e 26 (ethylene). Ethanol contributions have been subtracted from the m/e = 26 peak.

Figure 2. Thermal desorption spectrum of ethanol on MgO contaminated by species from stainless steel. — — — m/e 31 (ethanol), --- m/e 18 (water), —— m/e 26 (ethylene). Ethanol contribution have been subtracted from the m/e=26 peak.

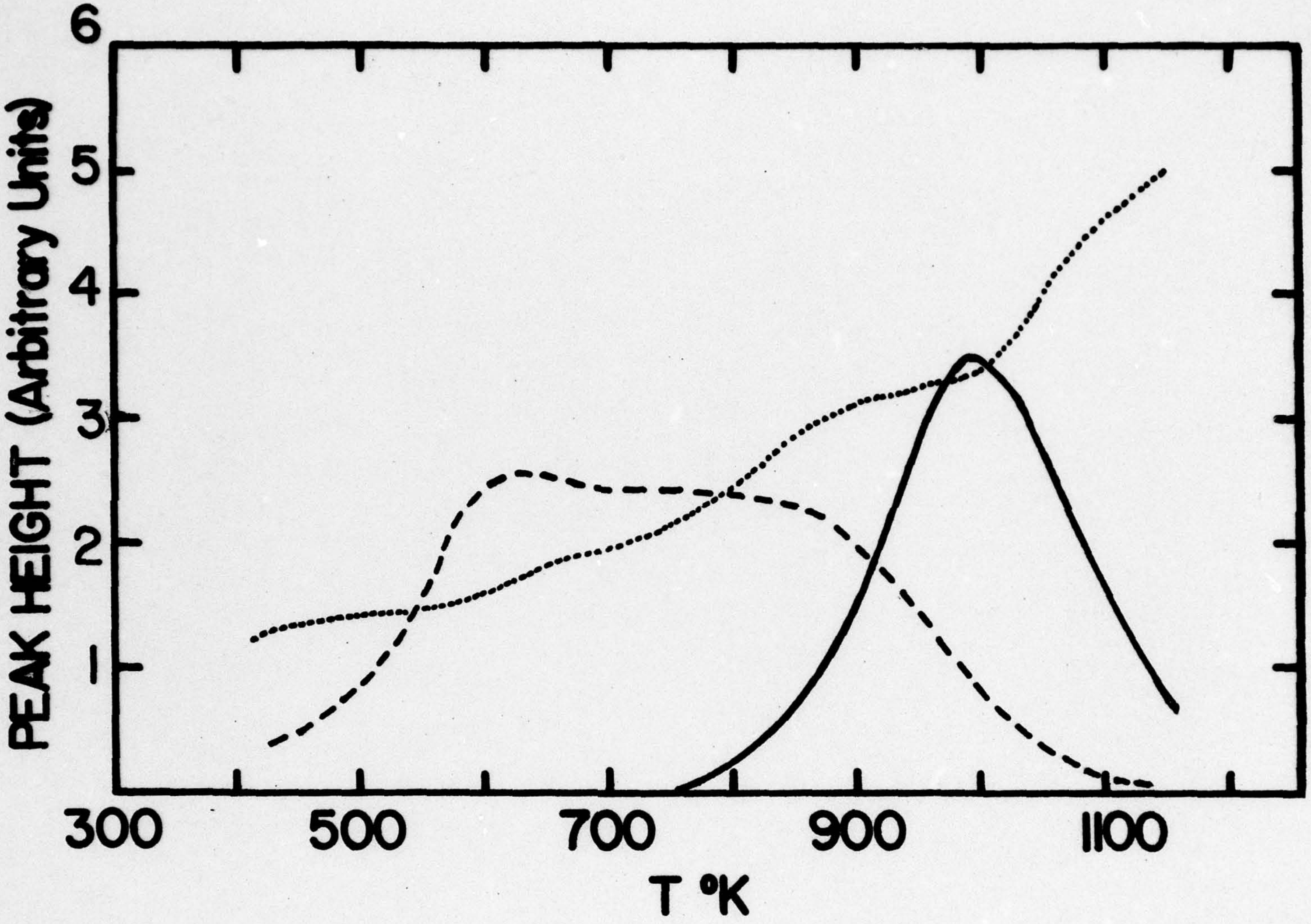
Figure 3. Thermal desorption spectrum of ethanol on MgO doped with NiO. The legend is the same as for figure 1.

Figure 4. Steady state production of ethylene at various temperatures. Ethanol was continuously leaked into the system at a constant rate with an initial pressure of 5 x 10^{-7} torr. The solid lines represent the ratio (m/e 26 peak height)/(m/e 31 peak height), while the dashed line represents this ratio for ethanol fragmentation in the mass spectrometer.

Figure 5. Steady state production of ethylene with deuterated ethanol pre-adsorbed on the surface. The dashed lines are the m/e 34 peak heights and represent C_2D_4 desorbing from the surface. The solid lines are the m/e 26 peak heights (corrected for ethanol contributions) which represent C_2H_4.

Figure 6. Thermal desorption spectrum of acetic acid dsorbed on pure MgO. The dashed line represents the desorption of acetic acid, while the solid lines represent the major mass peaks of another desorbed species (m/e 41 and m/e 13 were minor peaks) identified by its mass spectrum

as ketene. (m/e 28 is the total signal, with contributions from acetic acid and ketene.)



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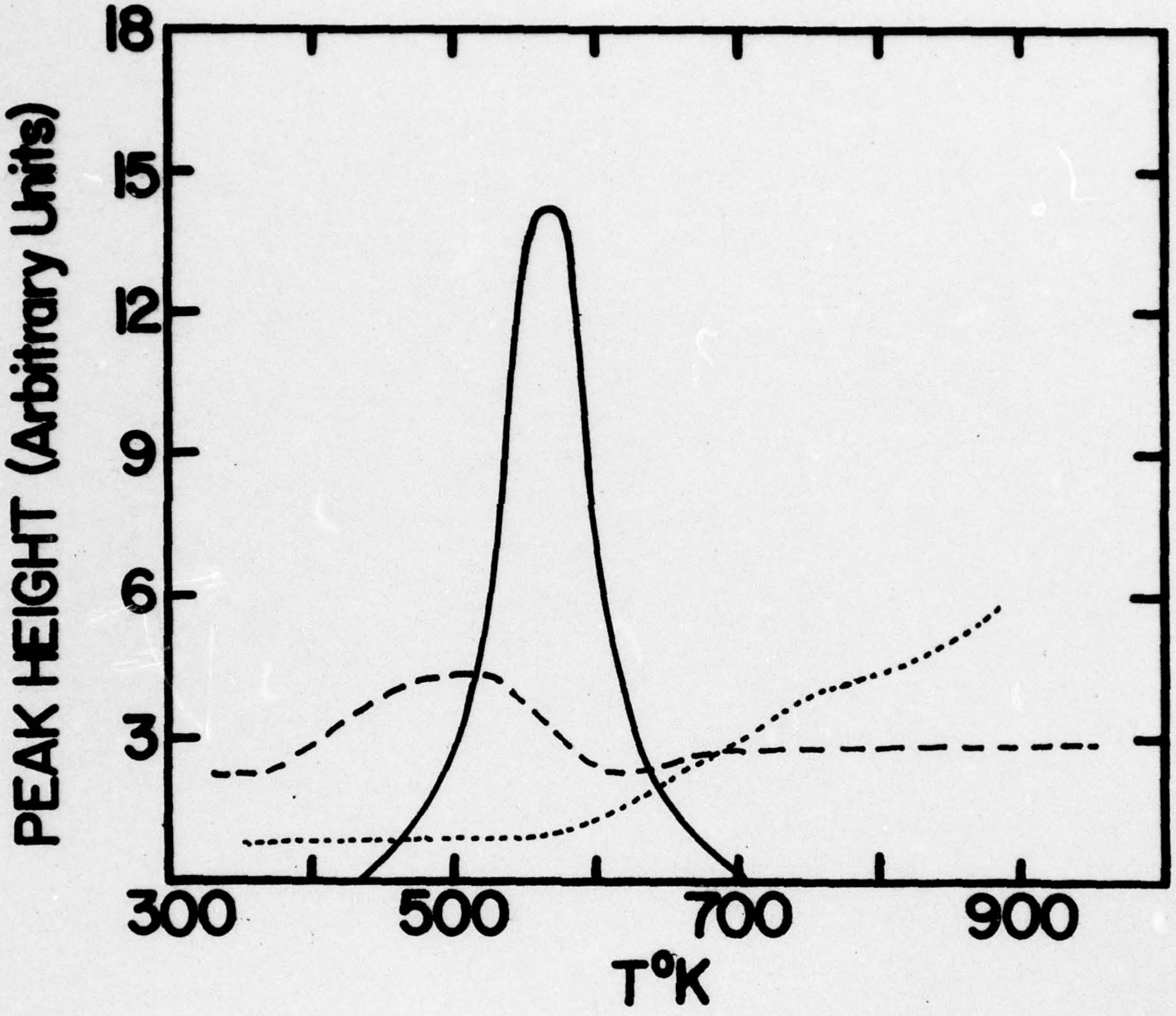

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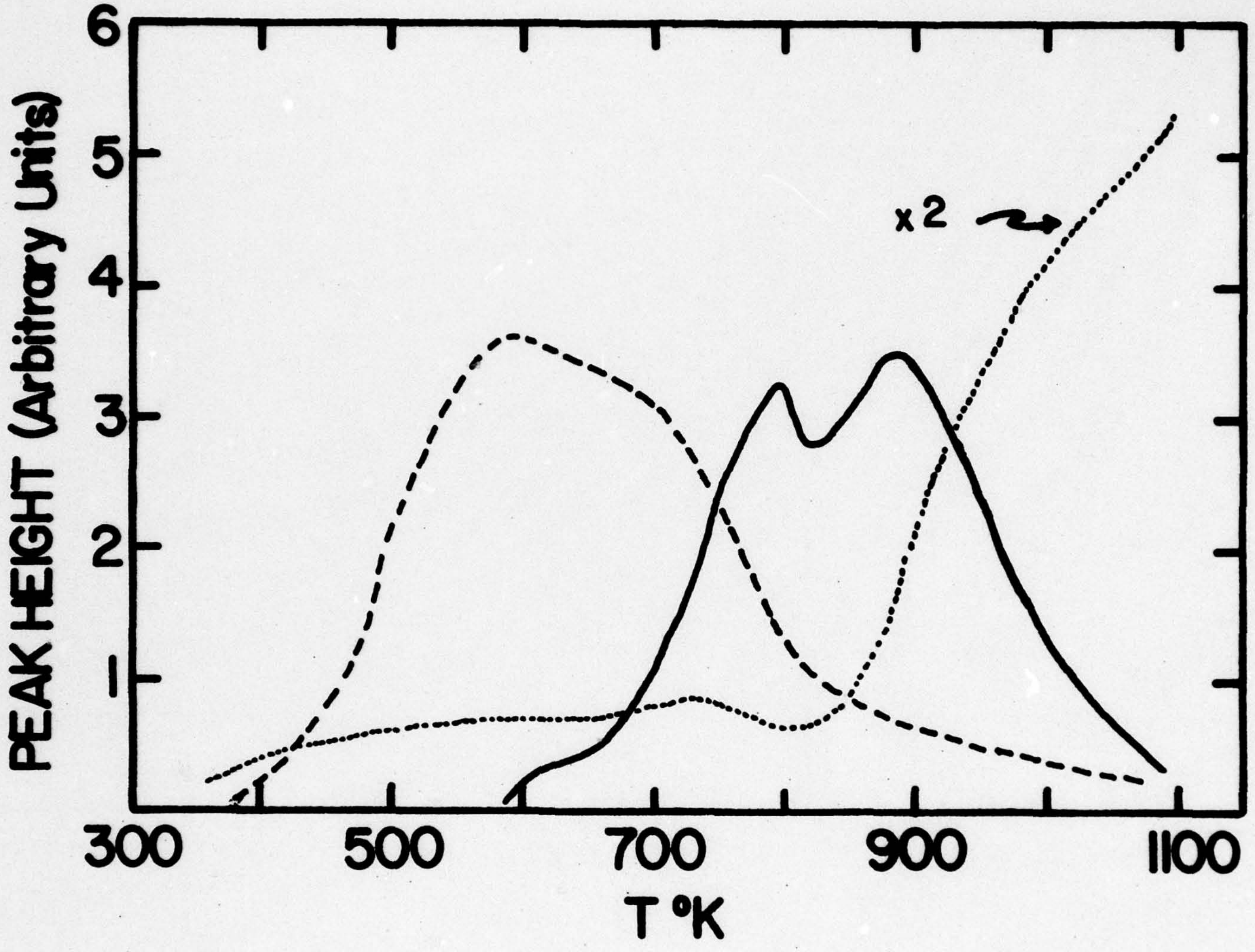
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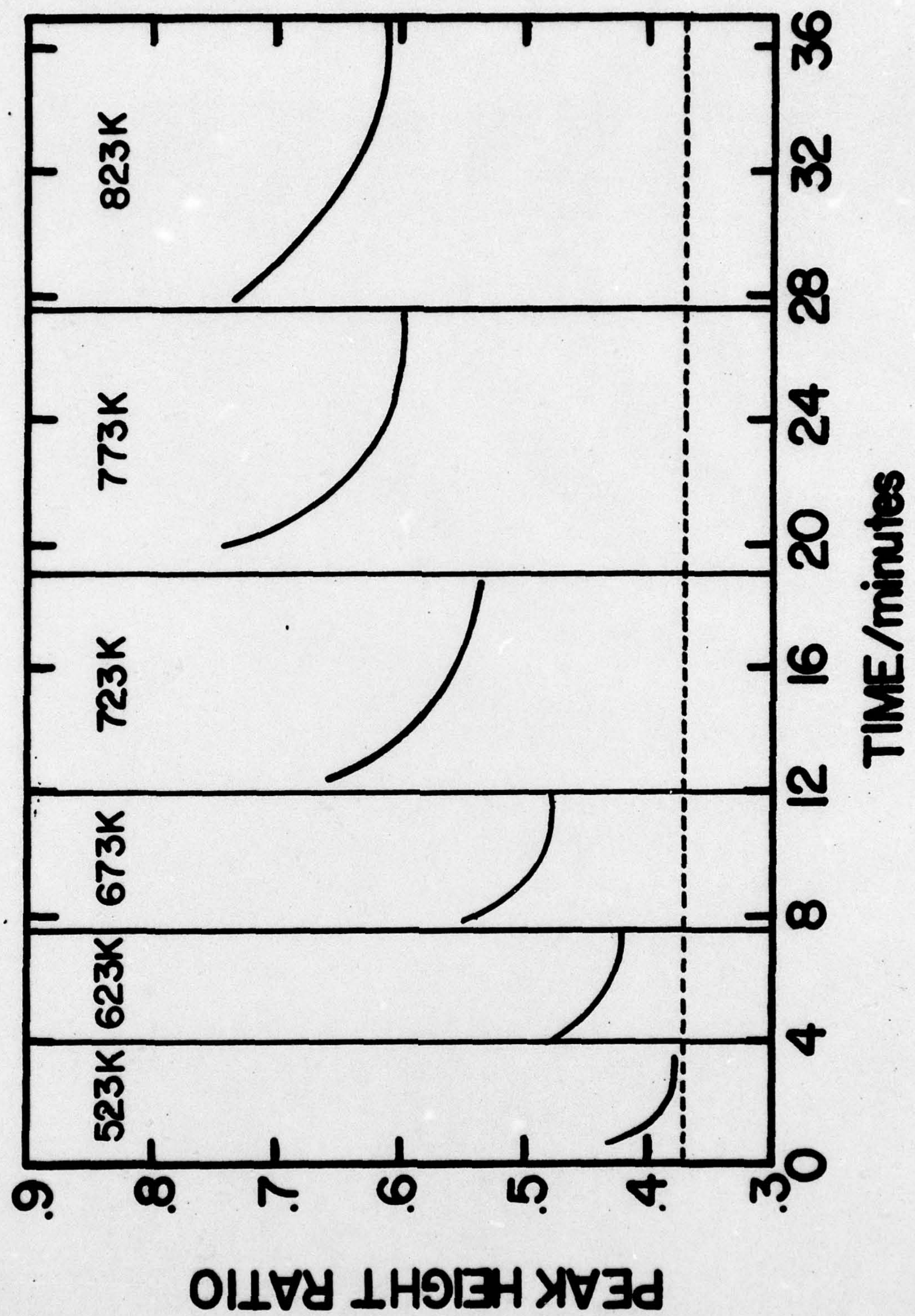
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Figure 4.

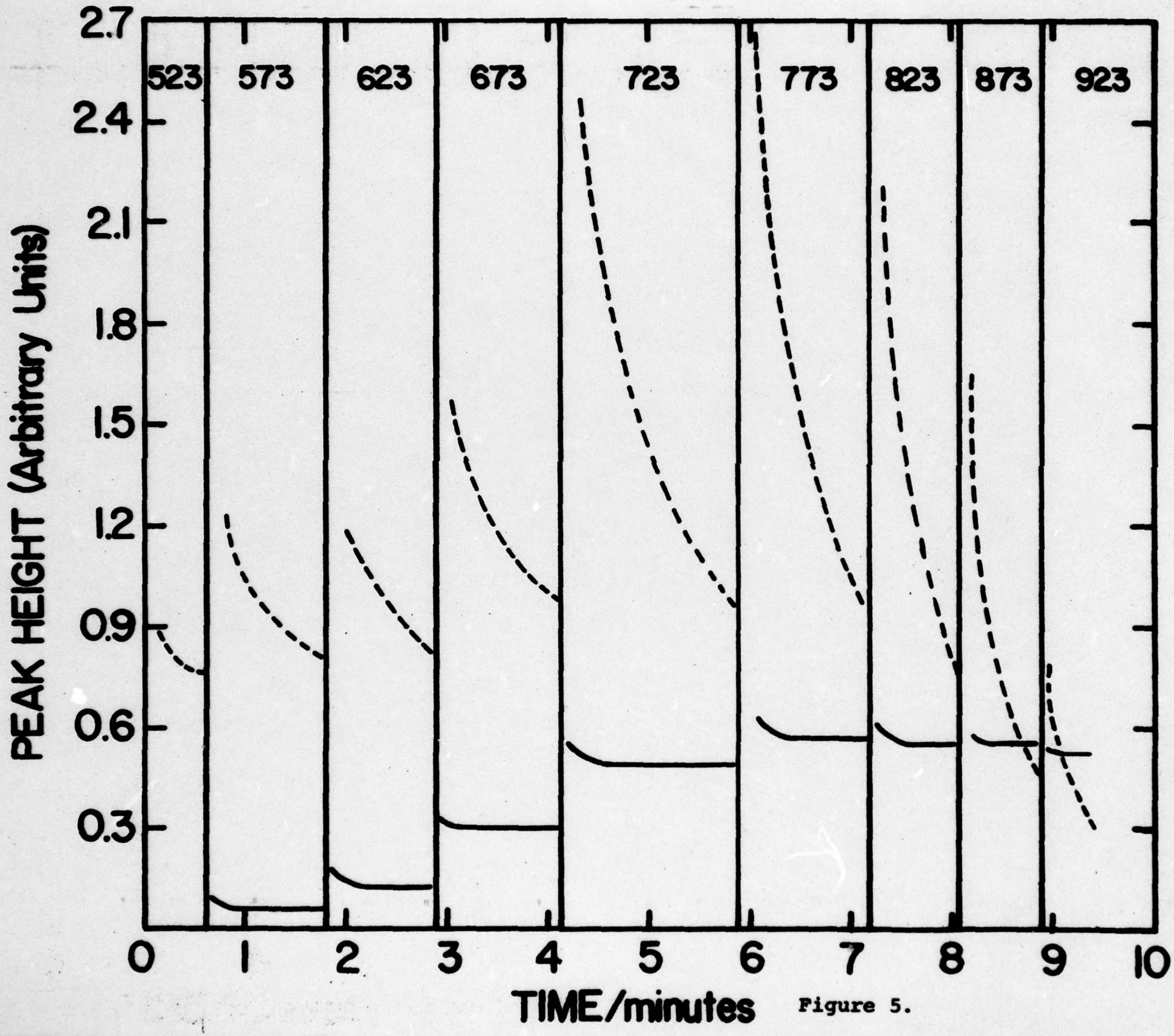
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Figure 5.

4

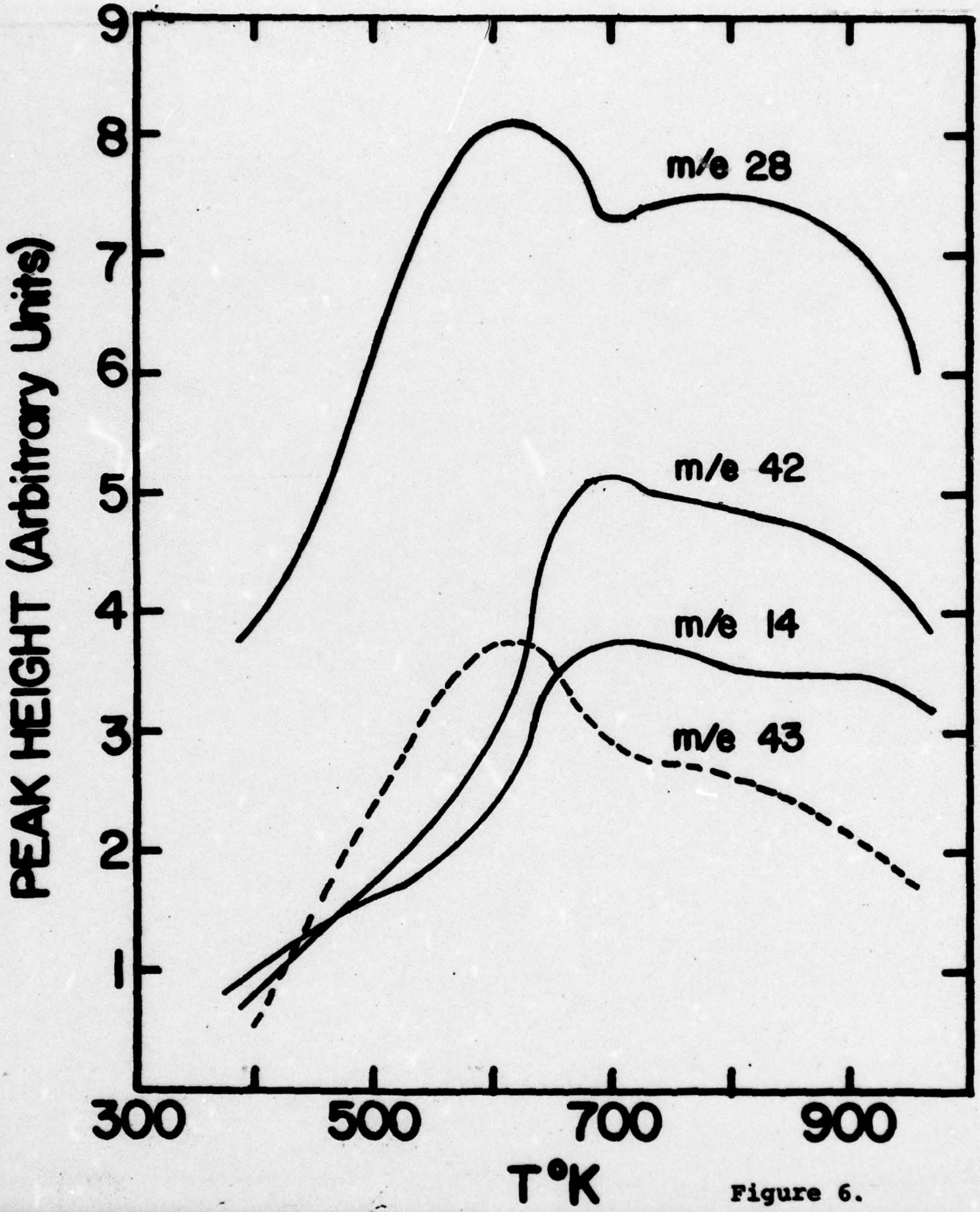
m/e 28
m/e 42
m/e 14
m/e 43
PEAK HEIGHT (Arbitrary Units)
9
8
7
6
5
4
3
2
1
300
500
700
900
T°K

Figure 6.