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## 19. ABSTRACT (continued)

The efficiency of  $\text{CH}_3\text{O}$  formation in the reactions of F and OH radicals with  $\text{CH}_3\text{OH}$  has been probed via product studies of the former reaction and via rate constant measurements of several isotopic variants of the latter reaction. Values of the branching fraction for  $\text{CH}_3\text{O}$  formation of respectively  $0.75 \pm 0.10$  and  $0.15 \pm 0.08$  were obtained. Rate constants of the  $\text{CH}_3\text{O} + \text{NO}$  reaction have been measured over a range of pressure and temperature. For the combination channel, the limiting low pressure rate constant is deduced to be  $(2.9 \pm 0.3) \times 10^{-29} (T/300)^{-2.5 \pm 1.0} \text{ cm}^6 \text{ s}^{-1}$ ; for the bimolecular abstraction channel (yielding  $\text{CH}_2\text{O} + \text{HNO}$ ), the value is  $(7.9 \pm 1.0) \times 10^{-13} \exp[(400 \pm 40)/T] \text{ cm}^3 \text{ s}^{-1}$ . The products of both channels have been detected, establishing that atom transfer is the major channel at low pressure.

Initial measurements suggest that the reaction of  $\text{CH}_3\text{O}$  with H atoms is extremely fast,  $k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ; the reaction of  $\text{CH}_3\text{O}$  with O atoms is significantly slower, with  $k \sim (3-10) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ .

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## 1. Introduction

Most reactions between stable molecules in the gas phase occur via a sequence of simple reaction steps, involving highly reactive radicals. Knowledge of the rates and products of such elementary reactions are needed for successful modeling of any complex reaction system, including those in the natural and perturbed atmosphere and combustion and laser systems. While much is known about reactions involving H-atom abstraction, which includes reactions of e.g. H, O, OH and Cl with stable molecules, reactions occurring via a strongly-bound intermediate are much less well characterized. A major aspect of this project was to obtain reliable rate constants for the combination reaction:



over a wide range of temperature and for several third bodies, for use in modeling combustion systems. Following this study, attention turned to the formation and reactions of the CH<sub>3</sub>O radical, as a continuation of a previous study of its reaction with NO<sub>2</sub>.<sup>1</sup> The reactions of OH and F with CH<sub>3</sub>OH were examined as sources of CH<sub>3</sub>O and showed interesting contrasts in behavior. The reaction of CH<sub>3</sub>O with NO was studied in detail, via rate constant measurements over a range of pressure and temperature and an investigation of two product channels. A study of the reactions of CH<sub>3</sub>O with O and H atoms was commenced; both reactions appear to be very fast. Each of these systems is described further below.

The grant was originally awarded to Professor F. Kaufman (d. July 1985). For the remainder of the grant period, Professor M. Golde acted as principal investigator. The other personnel involved were Dr. J. L. Durant (post-doctoral associate and research assistant professor) and the following graduate students:

K-J. Hsu (Ph.D. 1986), J. A. McCaulley (Ph.D. 1987), N. Kelly (M.Sc. 1986) and A. M. Moyle.

## 2. Experimental Techniques

Most of the studies were carried out in two discharge-flow apparatuses. One system (system "A")<sup>2</sup> was designed specifically for the relatively high pressures needed for the H + O<sub>2</sub> study and was operated in the range 4 - 70 Torr, with He as the principal carrier gas. H atoms were produced initially via a thermal dissociator. When studying reaction (1) at elevated temperatures, however, the large background of undissociated H<sub>2</sub> participated significantly in interfering secondary reactions. For such studies, the thermal dissociator was replaced by a conventional microwave discharge, which achieved much higher fractional dissociation of the H<sub>2</sub> and thus permitted use of much lower H<sub>2</sub> concentrations. The H-atom stream in He carrier gas was added to the main carrier gas, which consisted either of pure He or mixtures of N<sub>2</sub> (mole fraction 0.27 - 0.74) or H<sub>2</sub>O (mole fraction 0.049 - 0.26). O<sub>2</sub> was added further downstream through a movable inlet.

At the downstream end of the flow tube, the gas was expanded via a 0.35 mm diameter orifice into a lower-pressure detection chamber. The principal detection technique was atomic resonance fluorescence, for relative concentration measurements of the H atoms. Another detection port allowed simultaneous detection of OH (and of HO<sub>2</sub> by chemical conversion to OH) by molecular resonance fluorescence.

For experiments at elevated temperatures, a heating mantle encasing the flow tube was used. To minimize wall loss of radicals, the flow tube was coated with halocarbon wax. Above 370K, melting of the wax prevented its use and the tube was rinsed with HF and distilled H<sub>2</sub>O. Wall loss rates under these

conditions were very small,  $< 3 \text{ s}^{-1}$  for H atoms and  $\sim 15 \text{ s}^{-1}$  for OH radicals.

The other discharge-flow apparatus ("B")<sup>3</sup> operates at normal pressures, 0.5 - 5 Torr with He or Ar carrier gas. Radicals are produced either by pulsed infra-red multi-photon dissociation of precursor molecules, or by microwave discharge of suitable gases followed by rapid chemical conversion to the species of interest. The latter method was used for the studies described here. Three detection techniques are available with this system. Firstly, resonance-fluorescence has been used for detection of OH radicals and of H atoms (by chemical conversion to OH). Secondly, laser-induced fluorescence (Lambda-Physik EMG103MSC, FL 2001) is used for detection of OH and CH<sub>3</sub>O and deuterated analogs. Finally, molecular-beam-sampled mass spectrometry is used for characterization of reaction products, including HF, DF and CH<sub>3</sub>ONO.

All kinetic measurements were performed under pseudo first-order conditions. The exponential decay of the minor species was monitored as a function of reaction time to yield the effective first order rate coefficient. Runs were repeated over a range of concentrations of the major species to yield the second-order rate constant. Standard corrections were applied where necessary for wall loss and for radial or axial diffusion effects.

### 3. H + O<sub>2</sub> + M

The reaction between H and O<sub>2</sub> can occur via two channels:



The rates of these channels have widely different temperature dependences and competition between them helps determine the second explosion limit of the H<sub>2</sub>/O<sub>2</sub>

reaction. The aim of the present study was to obtain reliable data over the temperature range 298 to 1000K, in order to bridge the gap between previous low temperature (200-400K) and high temperature (>950K) studies. He (the main bath gas), N<sub>2</sub> and H<sub>2</sub>O were examined as third bodies, M.

Under all conditions, the concentration relationship  $[M] \gg [O_2] \gg [H]$  was maintained. Briefly, the decay of  $[H]$  as a function of reaction time yielded an effective first order rate coefficient,  $k^I$ . Values of  $k^I$ , measured as a function of  $[O_2]$ , yielded a second-order rate constant,  $k^{II}$ .  $k^{II}$  was determined at several values of  $[M]$  to yield the true third-order rate constant,  $k^{III}$ , of reaction (1).

In practice, the plots of  $k^I$  vs  $[O_2]$  were not accurately linear, due to the effect of secondary reactions initiated by:



for which the branching fractions,  $f$ , are respectively  $0.87 \pm 0.04$ ,  $0.04 \pm 0.02$  and  $0.09 \pm 0.04$ .<sup>4</sup> At each value of  $[M]$ , a mechanism comprising 10 reaction steps was analyzed,<sup>2</sup> with  $k^{II}$  varied to obtain the best fit to the experimental  $k^I$ . An example of the experimental and calculated  $k^I$  is shown in Figure 1. Plots of the resulting  $k^{II}$  as a function of  $[M]$  for  $M = He, N_2$  and  $H_2O$  are shown in Figures 2-4. The  $k^{III}$  values obtained were 10-50% lower than those derived by neglecting secondary chemistry.

The study of the  $H + O_2$  reaction at elevated temperatures followed a similar procedure. As the temperature is increased, atom transfer to yield  $OH + O$  becomes increasingly important, and it was concluded that, above about

700K, the observed H-atom decay is dominated by this channel, rather than by the combination channel, even at the highest total pressure, 70 Torr, attainable in this system. The study was, therefore, terminated at ~640K.

Our measurements yielded the following third-order rate constants at 298K:

$$k^{III}(M = \text{He}) = (2.6 \pm 0.2) \times 10^{-32} \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(M = \text{N}_2) = (6.1 \pm 0.9) \times 10^{-32} \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(\text{H}_2\text{O}) = (6.4 \pm 0.8) \times 10^{-31} \text{ cm}^6\text{s}^{-1}.$$

Over the temperature range 298 - 639K, we determined:

$$k^{III}(\text{He}) = (4.0 \pm 1.2) \times 10^{-33} \exp[(560 \pm 100)/T] \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(\text{N}_2) = (6.5 \pm 2.2) \times 10^{-33} \exp[(680 \pm 110)/T] \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(\text{H}_2\text{O}) = (1.9 \pm 0.9) \times 10^{-32} \exp[(1050 \pm 140)/T] \text{ cm}^6\text{s}^{-1}.$$

The data at room temperature agree well with several earlier investigations.<sup>5-7</sup> In other studies, incorrect assumptions concerning the rates of secondary reactions were made; reanalysis, using currently-available rate data, yields values close to those presented here. Averaging the available data, we propose the following rate constants at 298K:

$$k^{III}(\text{He}) = (2.5 \pm 0.1) \times 10^{-32} \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(\text{N}_2) = (6.3 \pm 0.7) \times 10^{-32} \text{ cm}^6\text{s}^{-1}$$

$$k^{III}(\text{H}_2\text{O}) = (6.3 \pm 0.8) \times 10^{-31} \text{ cm}^6\text{s}^{-1}.$$

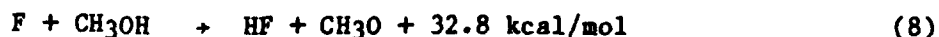
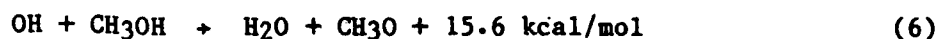
The complete set of the present data is plotted in Arrhenius form in Figure 5, together with previous high temperature values. Such data for M = Ar cluster

closely around the extrapolation of the present data for M = He, consistent with the similar M-efficiencies of He and Ar at room temperature. The rates for N<sub>2</sub> are somewhat smaller than extrapolation of the present data, but the ratio  $k_{III}(N_2)/k_{III}(Ar)$  determined at 1050K by Slack<sup>8</sup> agrees well with our prediction. The discrepancies in the literature values for  $k_{III}(H_2O)$  at high temperature<sup>9,10</sup> prevent a critical comparison with an extrapolation of the present data. In summary, the present data have established that the room temperature and high temperature data can be bridged via Arrhenius expressions for the rate constants.

The data show H<sub>2</sub>O to be a much more efficient third body than either He or N<sub>2</sub>. This is ascribed to the greater efficiency of H<sub>2</sub>O at stabilizing the initially-formed hot HO<sub>2</sub>\* species via energy transfer in collisions; this M effect has been observed previously in several other combination reactions. As the temperature is raised, the difference in M efficiencies of He and H<sub>2</sub>O decreases somewhat.

#### 4. The Reactions of F and OH with CH<sub>3</sub>OH.

These reactions were initially investigated in order to assess their potential as sources of methoxy radicals, CH<sub>3</sub>O; however, they were found to be sufficiently interesting to warrant a more extended study. In each reaction, H-atom abstraction from either end of the CH<sub>3</sub>OH molecule is possible, but with different exothermicities:



In the first reaction, it has been found that the more exothermic channel is strongly favored. However, the product distribution from the second reaction, which occurs at close to the collision rate, is very uncertain, literature values for the branching fraction for the channel leading to CH<sub>3</sub>O ranging between  $0.3 \pm 0.1$  and  $0.63 \pm 0.07$  (See Table 1). In the present study, the branching fraction for this reaction was investigated by a more direct method than those used previously; and the rate constants of several isotopic variants of the OH + CH<sub>3</sub>OH reaction were determined at room temperature, yielding new insight into this reaction.

Channels (8) and (9) were investigated by mass spectrometry in apparatus "B" by comparing the yields of HF and DF from the reactions of F with CH<sub>3</sub>OD or CD<sub>3</sub>OH, e.g.



Signals at *m/e* 20(HF) and 21(DF) were measured over a concentration range, [methanol]/[F], of 2 to 80, a total carrier gas pressure of 0.5 - 2 Torr and with both wax-coated and uncoated flow tubes. Consistent results were obtained, yielding branching fractions for methoxy formation of  $0.81 \pm 0.07$  from CH<sub>3</sub>OD and  $0.69 \pm 0.08$  from CD<sub>3</sub>OH. This difference is not considered significant and it is concluded that kinetic isotope effects are quite small for this reaction, in agreement with previous findings.<sup>11,12</sup> This is confirmed by a very recent study,<sup>11</sup> which additionally finds a CH<sub>3</sub>O branching fraction of  $\sim 0.62$ , in support of our value. The branching fractions are summarized in Table 1.

In the OH + CH<sub>3</sub>OH study, OH (OD) was formed by the rapid reaction of H (D) with NO<sub>2</sub>, and detected by laser-induced fluorescence using the OH(A<sup>2</sup>Σ<sup>+</sup> - X<sup>2</sup>Σ<sup>+</sup>)

transition. Concentration ratios, [methanol]/[hydroxyl], were kept sufficiently large for possible secondary reactions of OH with reaction products to be unimportant.

Measured bimolecular rate constants for 7 isotopic variants of the OH + CH<sub>3</sub>OH reaction are summarized in Table 2. The value for OH + CH<sub>3</sub>OH itself agrees well with previous data. No other data for the reactions of the deuterated species appear to be available. Deuteration of the methyl group causes a large decrease in the rate constants, while deuteration of the hydroxyls has a much smaller effect. If it is assumed that primary isotope effects (i.e. in the bond to be broken) are much larger than secondary effects due to substitution in other bonds, then the results imply that channel (7) predominates over (6), and a simple model<sup>13</sup> yields a branching fraction of 0.15 ± 0.08 for CH<sub>3</sub>O formation in the OH + CH<sub>3</sub>OH reaction, in good agreement with earlier measurements.

It is concluded that the branching in the reactions of F and OH with CH<sub>3</sub>OH differs markedly, with the rapid F reaction (which has a negligible activation energy) strongly favoring the less exothermic channel. It is interesting that both UV photodissociation of CH<sub>3</sub>OH and the reaction of electronically-excited N<sub>2</sub> in the (A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) state with CH<sub>3</sub>OH also favor cleavage of the CH<sub>3</sub>-H bond. In contrast, H-CH<sub>2</sub>OH cleavage is dominant in the reaction of Cl with CH<sub>3</sub>OH; however, abstraction of the hydroxyl H atom is endothermic in this case.

### 3. Investigation of the reaction CH<sub>3</sub>O + NO.

This reaction is of possible importance in polluted atmospheres and is of direct relevance to the decomposition of CH<sub>3</sub>ONO, a model propellant. The reaction is of interest as it offers the possibility of two competing channels:



The latter channel may occur via two possible mechanisms: either direct abstraction of H from CH<sub>3</sub>O, or unimolecular decomposition of the intermediate CH<sub>3</sub>ONO. We have measured the second-order rate constant of the overall reaction over the pressure range (M = He, Ar) 0.75 - 5 Torr and the temperature range 223 - 473K. The reaction products have been examined over a smaller range of conditions. For the kinetic measurements, CH<sub>3</sub>O radicals were produced by two separate reactions:



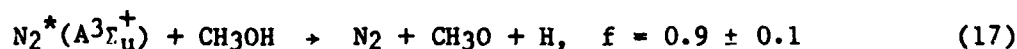
In each case, F atoms were produced by discharging a dilute mixture of F<sub>2</sub> in He. CH<sub>3</sub>O was detected by LIF in the (A<sup>2</sup>A<sub>1</sub> - X<sup>2</sup>E) band system, utilizing lines in the 3<sub>0</sub><sup>2</sup> band at 303.8 nm. Initial concentrations of CH<sub>3</sub>O in the reaction zone were typically < 5 x 10<sup>11</sup> cm<sup>-3</sup>.

In the presence of NO, CH<sub>3</sub>O decayed exponentially over a concentration range of at least 10, but often flattened out at large reaction times, indicative of a secondary process forming CH<sub>3</sub>O radicals. The source was not definitely identified, but heterogeneous processes are suspected. Kinetic data were derived from the linear portions of the plots of ln(I<sub>LIF</sub>) vs reaction time. Typical decay curves are shown in Fig. 6, and a plot of the first order rate coefficient vs [NO] in Fig. 7. The resulting second-order rate coefficient

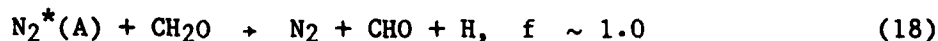
increases slightly with pressure between 1 and 5 Torr, and decreases significantly with increasing temperature between 200 and 450K, as illustrated in Fig. 8.

The products of this reaction were investigated in two ways.  $\text{CH}_3\text{ONO}$  was detected via mass spectrometry at  $m/e$  61 (parent) and 60. The signal was calibrated using pure  $\text{CH}_3\text{ONO}$ . A small correction was applied for  $\text{CH}_3\text{NO}_2$ , detected as a minor product of the  $\text{CH}_3 + \text{NO}_2$  precursor reaction, equ. 15. [It was concluded that the branching fraction for  $\text{CH}_3\text{NO}_2$  formation was  $0.040 \pm 0.004$  at 0.5 Torr total pressure, and  $0.07 \pm 0.02$  at 1 Torr]. For the  $\text{CH}_3\text{O} + \text{NO}$  reaction, the branching fractions for  $\text{CH}_3\text{ONO}$  formation were  $0.11 \pm 0.02$  (0.52 Torr, 298K),  $0.20 \pm 0.05$  (1.0 Torr, 298K) and  $0.16 \pm 0.05$  (1.0 Torr, 223K).

A brief search for  $\text{HNO}$ , a product of the other channel of this reaction, equ. 13, was not successful in this apparatus. Therefore, the reaction was studied in another flow system, with  $\text{CH}_3\text{O}$  formed by the reaction:<sup>14</sup>



$\text{HNO}$  was readily detected via LIF in the ( $\text{A}^1\text{A}'' - \text{X}^1\text{A}'$ ) band system. The signal was compared with that from the reaction sequence:



This study confirmed that the yield of  $\text{HNO}$  in reaction (12,13) is large at low pressures. Quantitative comparison with the  $\text{CH}_3\text{ONO}$  measurements awaits characterization of possible wall loss of  $\text{CHO}$  and  $\text{CH}_3\text{O}$  between the  $\text{N}_2(\text{A})$  and  $\text{NO}$  inlet points.

The measured rate constants agree well with those of a previous study,<sup>15</sup> which spanned the pressure range 3 - 190 Torr. Deconvolution of the rate data

to yield rate constants for the recombination ( $k_{\text{rec}}$ ) and atom transfer ( $k_{\text{AT}}$ ) channels (equ. 12 and 13 respectively) is hampered by the fact that the combination channel cannot be assumed to be exhibiting limiting low pressure behavior even at the low pressures of this study. According to Lindemann-Hinshelwood theory, the effective second order rate coefficient,  $k^{\text{II}}$ , for this channel can be determined, given the limiting low pressure ( $k_{\text{O}}^{\text{III}}$ ) and high pressure ( $k_{\infty}^{\text{II}}$ ) rate constants.

$$k_{\text{rec}}^{\text{II}} = k_{\text{O}}^{\text{III}} k_{\infty}^{\text{II}} [M] / (k_{\text{O}}^{\text{III}} [M] + k_{\infty}^{\text{II}}) = k_{\text{LH}}, \quad (20)$$

where M is the buffer gas (Ar or He). However, this theory is oversimple and Troe<sup>16</sup> has suggested an amended expression which yields good agreement, for the fall-off behavior, with RRKM theory. This approach is attractive as, apart from  $k_{\infty}$ , the model essentially contains only one variable parameter,  $S_{\text{K}}$ , which can be readily estimated from the known fundamental vibration frequencies of  $\text{CH}_3\text{ONO}$ .

Using the measured high pressure rate constant,<sup>15</sup>  $1.2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ , for  $k_{\infty}^{\text{II}}$  and applying this model, values of the rate constants for the two channels were determined by a least squares fit to the rate coefficients at room temperature:  $k_{\text{AT}} = (2.89 \pm 0.07) \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ , and  $k_{\text{rec},0}^{\text{III}} = (2.9 \pm 0.3) \times 10^{-29} \text{ cm}^6\text{s}^{-1}$ . In the absence of experimental information,  $k_{\infty}^{\text{II}}$  was assumed to be independent of temperature and  $k_{\text{O}}^{\text{III}}$  to vary as  $T^{-n}$ . A least squares fit to the complete set of rate data (223 - 473K) yielded  $n \sim -2.5 \pm 1.0$ . Thus, within the limits of the assumption concerning  $k_{\infty}^{\text{II}}$ , the following rate constants were derived:

$$k_{\text{rec},0}^{\text{III}} = (2.9 \pm 0.3) \times 10^{-29} (T/300)^{-2.5 \pm 1.0} \text{ cm}^6\text{s}^{-1} \quad (21)$$

$$k_{\text{AT}} = (7.9 \pm 1.0) \times 10^{-13} e^{(400 \pm 40)/T} \text{ cm}^3\text{s}^{-1}. \quad (22)$$

These predict branching fractions for the recombination channel of  $0.10 \pm$

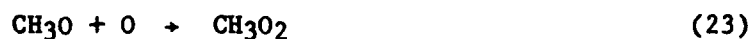
0.02 (297K, 0.5 Torr),  $0.17 \pm 0.02$  (297K, 1.0 Torr) and  $0.23 \pm 0.06$  (223K, 1.0 Torr), in fair agreement with the measured yields of  $\text{CH}_3\text{ONO}$ . At 4.0 Torr and 297K, the predicted HNO branching fraction is  $0.65 \pm 0.10$ , in moderate agreement with the uncorrected preliminary value of 0.3 - 0.4.

Previous studies have failed to establish the product distribution principally because  $\text{CH}_3\text{ONO}$  has been employed as the source of  $\text{CH}_3\text{O}$ . For instance, Sanders et al.<sup>17</sup> observed the kinetics of HNO formation to match those of  $\text{CH}_3\text{O}$  removal, whereas Zellner,<sup>15</sup> in a similar experiment, observed  $\text{CH}_2\text{O}$  formation to be limited to the photolysis pulse duration. Thus, while both studies observed HNO +  $\text{CH}_2\text{O}$  formation, the former group ascribed it to a channel of the  $\text{CH}_3\text{O} + \text{NO}$  reaction, but Zellner ascribed it to a channel of  $\text{CH}_3\text{ONO}$  photodissociation. Other investigations employed steady-state photolysis or thermal dissociation of  $\text{CH}_3\text{ONO}$  and are less direct; however, these found a small branching fraction of 0.10 - 0.15 for reaction (13) at high pressures.

The present study has demonstrated clearly that atom transfer is the major channel at low pressure. The inverse temperature dependence for this channel (which is evident from Fig. 3 and is independent of the way in which the recombination channel is modeled) suggests strongly that this channel occurs mainly via decomposition of the energetic  $\text{CH}_3\text{ONO}$  intermediate rather than via direct abstraction of a H atom. Thus, the rate coefficient for this channel should become smaller at high pressure, because of competitive collisional stabilization of the intermediate. Our findings are qualitatively in agreement with previous studies. A more quantitative comparison could be achieved by RRKM calculations which, however, require considerable information concerning the potential energy surface for this reaction.

## 6. The Reactions of CH<sub>3</sub>O with O and H atoms.

This project is continuing beyond the end of this grant period. Although the results are incomplete, they are sufficiently interesting to warrant this brief report. Radical-radical reactions, involving carbonaceous species, are expected to occur at close to the collision rate and they may be important in combustion systems. The reactions of CH<sub>3</sub>O with H and O atoms may occur via strongly-bound intermediates and have available more than one reaction channel:



CH<sub>3</sub>O is produced by reaction of F with CH<sub>3</sub>OH, using a discharge through dilute mixtures of F<sub>2</sub> or CF<sub>4</sub> in He as the source of the F atoms. CH<sub>3</sub>O is monitored by LIF. O or H atoms are produced in excess by discharging respectively O<sub>2</sub> or H<sub>2</sub>. The absolute O-atom concentration is measured via O + NO chemiluminescence, calibrated via the O + NO<sub>2</sub> titration technique. The absolute H atom concentration is measured by chemical conversion to OH, which is detected by resonance fluorescence.

In the initial stage of this investigation, the rate constants of the

reactions of CH<sub>3</sub>O with H and O at room temperature have been investigated. In both reactions, care has to be taken to achieve accurately exponential decays of the minor species CH<sub>3</sub>O as a function of reaction time. In the H-atom reaction, this was achieved by adding excess H<sub>2</sub>, presumably to remove any remaining (or newly-formed) F atoms in the reaction zone. Typical CH<sub>3</sub>O decays are shown in Figure 9; the preliminary rate constant is  $\sim 1 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ , three times larger than a previous estimate,<sup>18</sup> and only a factor of three below the collision rate. This rate constant is too high for combination, equ. (26), to be the major channel; the branching between the other channels is clearly of interest.

In the reaction of CH<sub>3</sub>O with O atoms, our preliminary rate constant is 3 to 10 times smaller than the previous measurement<sup>19</sup> of  $3 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ . Because of the rapidity of the CH<sub>3</sub>O + H reaction, careful modeling of the reaction with O will be required, because of the possible reaction sequence:



followed by reaction of CH<sub>3</sub>O with H. Clearly, the most reliable data will be expected at large initial [O]/[CH<sub>3</sub>O] concentration ratios. In the continuation of this study, rate constants over a range of temperature and carrier gas pressure will be determined, and the product channels will be investigated.

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Table 1: Methoxy yield of the F + methanol reaction

Reagent	Method <sup>a</sup>	$f_{\text{CH}_3\text{O}(\text{CD}_3\text{O})}$	Reference
CH <sub>3</sub> OD	HF,DF; IRCL	0.50	20
CH <sub>3</sub> OD	HF,DF; IRCL	0.31 ± 0.03	21
CH <sub>3</sub> OD	HF,DF; MS	0.3 ± 0.1	18
CD <sub>3</sub> OH	HF,DF; MS	0.5 ± 0.2	18
CH <sub>3</sub> OH	CH <sub>2</sub> OH; MS	0.59 ± 0.06	22
CH <sub>3</sub> OD	HF,DF; IRCL	0.38 ± 0.24	23
CD <sub>3</sub> OH	HF,DF; IRCL	0.63 ± 0.07	23
CH <sub>3</sub> OH	MS	0.60	11
CH <sub>3</sub> OD	MS	0.63	11
CD <sub>3</sub> OH	MS	0.61	11
CD <sub>3</sub> OD	MS	0.64	11
CH <sub>3</sub> OD	HF,DF; MS	0.81 ± 0.07	this work
CD <sub>3</sub> OH	HF,DF; MS	0.69 ± 0.08	this work

a. Methods: IRCL, infrared chemiluminescence; MS, mass spectrometry.

Table 2: Second-order rate coefficients of hydroxyl + methanol reactions

T = 298 ± 2 K

p = 3.00 ± 0.05 Torr

Reaction	$\bar{v}$ , a cm s <sup>-1</sup>	#b	10 <sup>13</sup> k <sub>II</sub> , cm <sup>3</sup> s <sup>-1</sup>
OH + CH <sub>3</sub> OH	931	6	9.7 ± 1.4
"	949	8	<u>10.5 ± 1.5</u>
"			AVE 10.1 ± 1.0
OD + CH <sub>3</sub> OH	549	8	9.5 ± 1.2
OD + CH <sub>3</sub> OD	468	8	9.3 ± 1.1
OH + CD <sub>3</sub> OH	449	14	3.35 ± 0.72
OD + CD <sub>3</sub> OH	449	8	2.86 ± 0.37
OH + CD <sub>3</sub> OD	951	8	1.34 ± 0.15
"	979	5	1.72 ± 0.21
"	463	6	2.22 ± 0.40
"	444	5	2.22 ± 0.30
"	674	9	<u>2.16 ± 0.28</u>
"			AVE 1.93 ± 0.45
OD + CD <sub>3</sub> OD	463	7	1.80 ± 0.33
"	444	8	1.57 ± 0.23
"	675	5	<u>1.64 ± 0.23</u>
"			AVE 1.67 ± 0.16

a. average bulk flow velocity

b. number of methanol concentrations

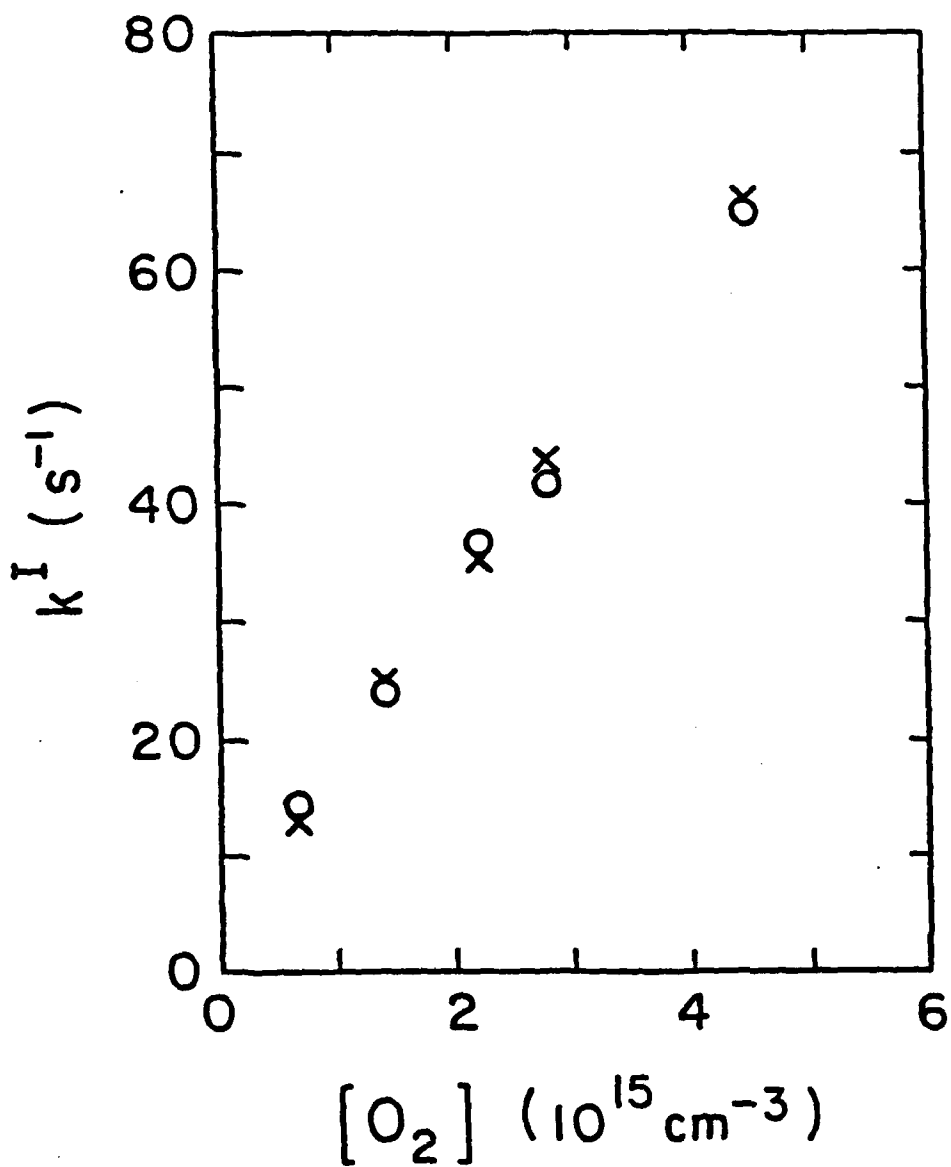


Figure 1

Plot of Pseudo-First Order Rate versus [O<sub>2</sub>]  
 for the Reaction H + O<sub>2</sub> + M at 5.3 torr.  
 ( He: 40.8%, N<sub>2</sub>: 59.2% ), O: experimental,  
 x: calculated;  $k_{\text{slope}} = 1.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ,  
 $k_{\text{calc.}} = 0.99 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ .

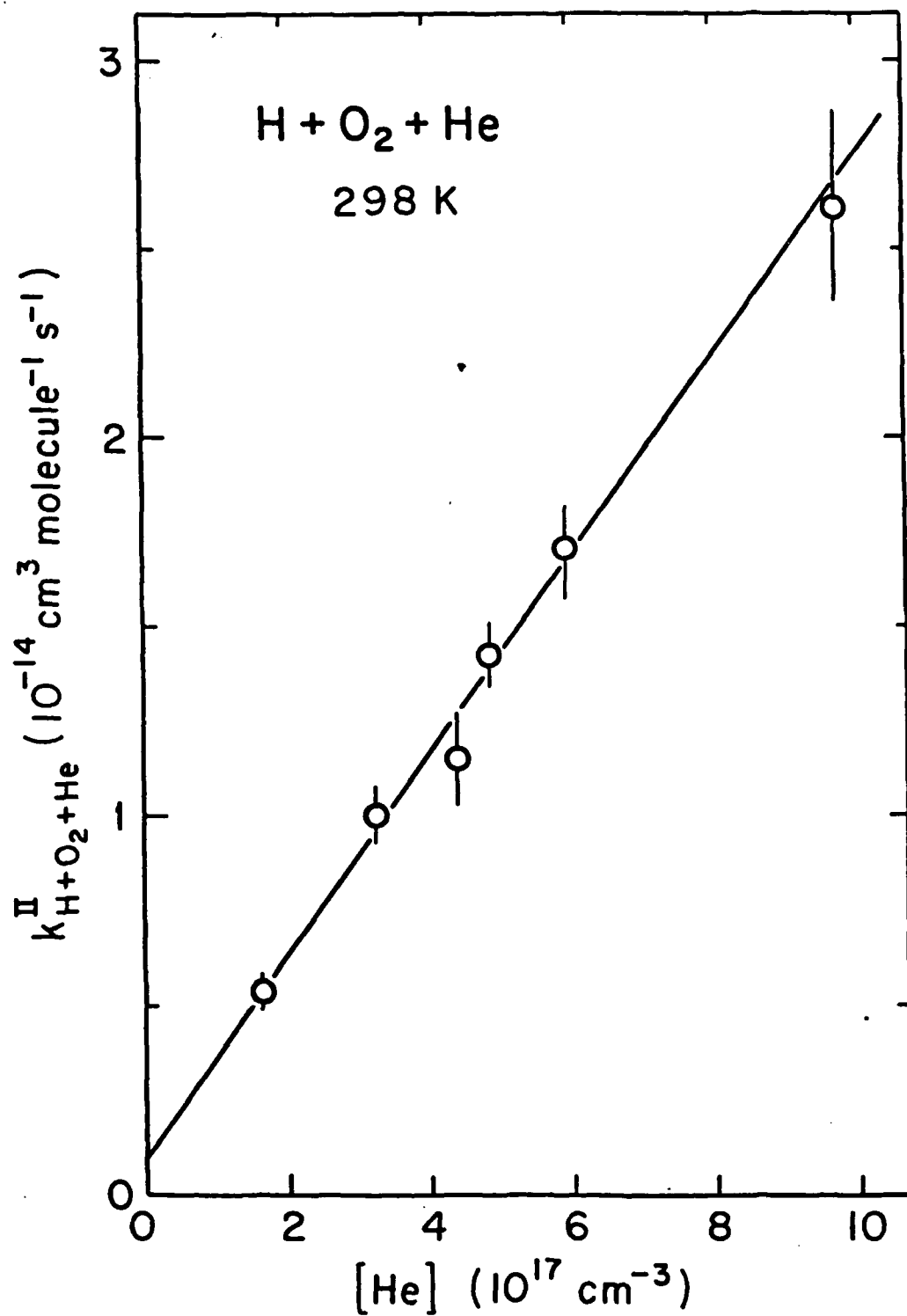


Figure 2. Plot of Pseudo-Second Order Rate Constant versus Helium Concentration at 298K.

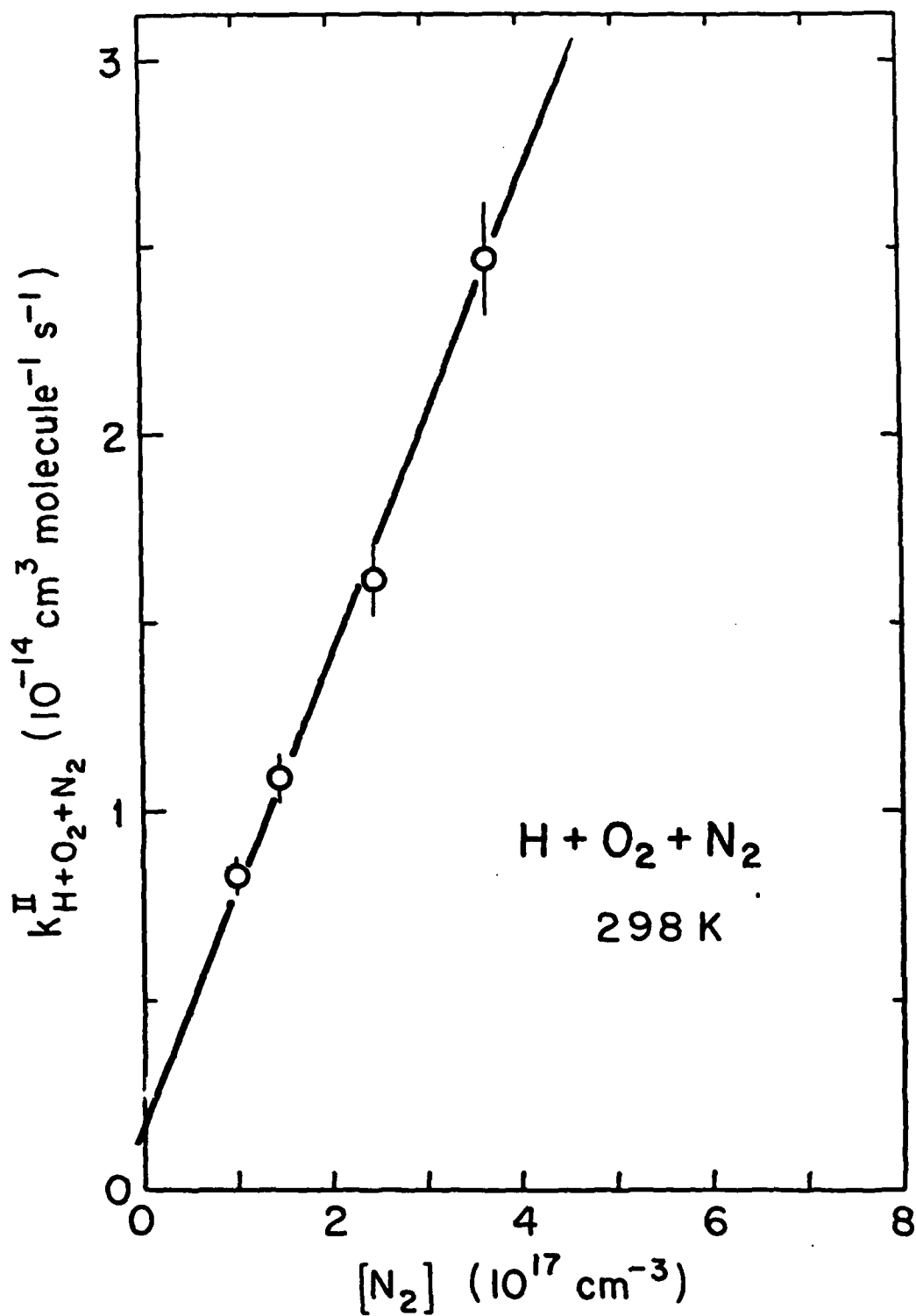


Figure 3.

Plot of Pseudo-Second Order Rate Constants versus  $N_2$  Concentrations for the Reaction  $H + O_2 + N_2$  at 298K.

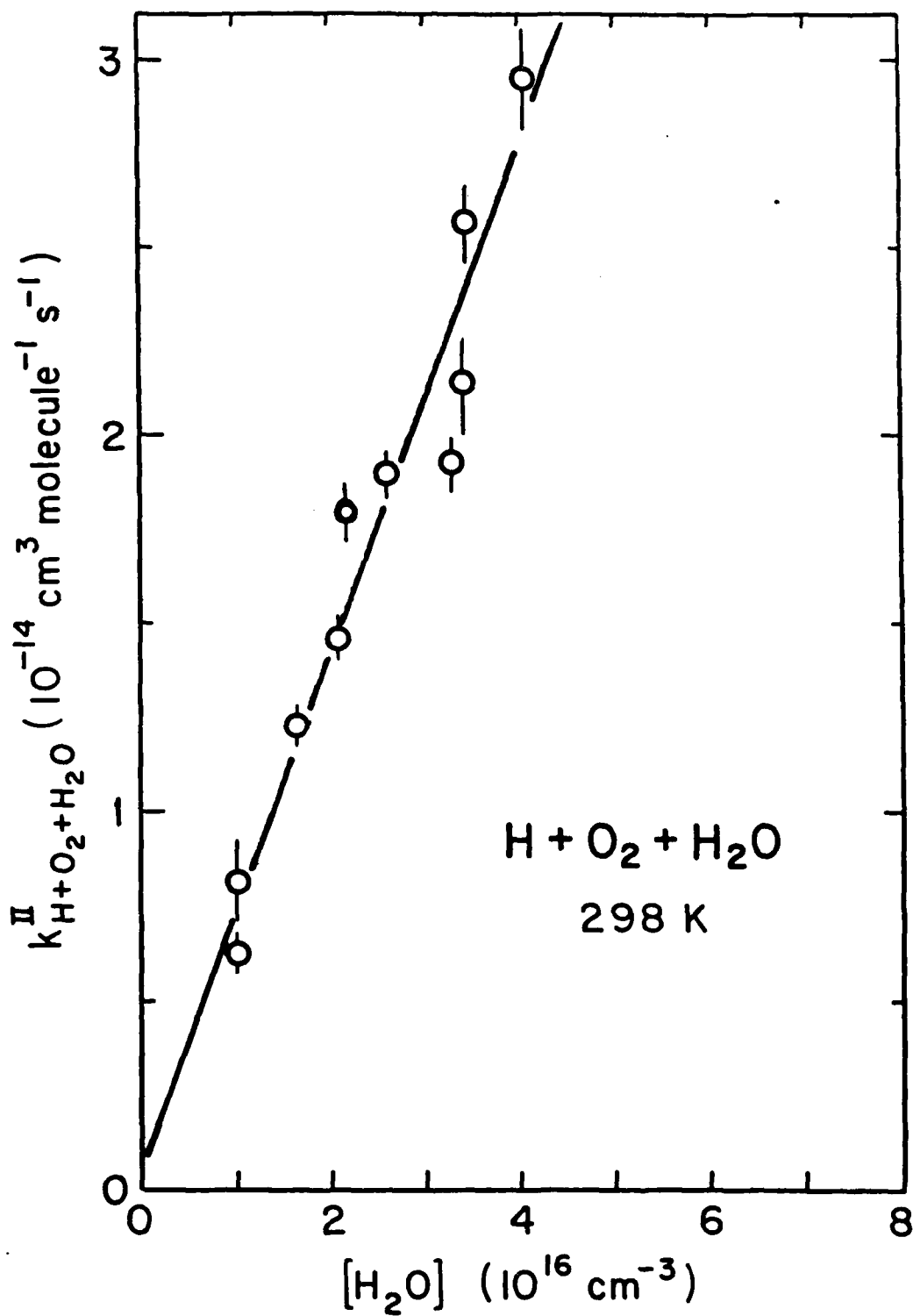


Figure 4. Plot of Pseudo-Second Order Rate Constant versus H<sub>2</sub>O Concentrations for the Reaction H + O<sub>2</sub> + H<sub>2</sub>O at 298 K.

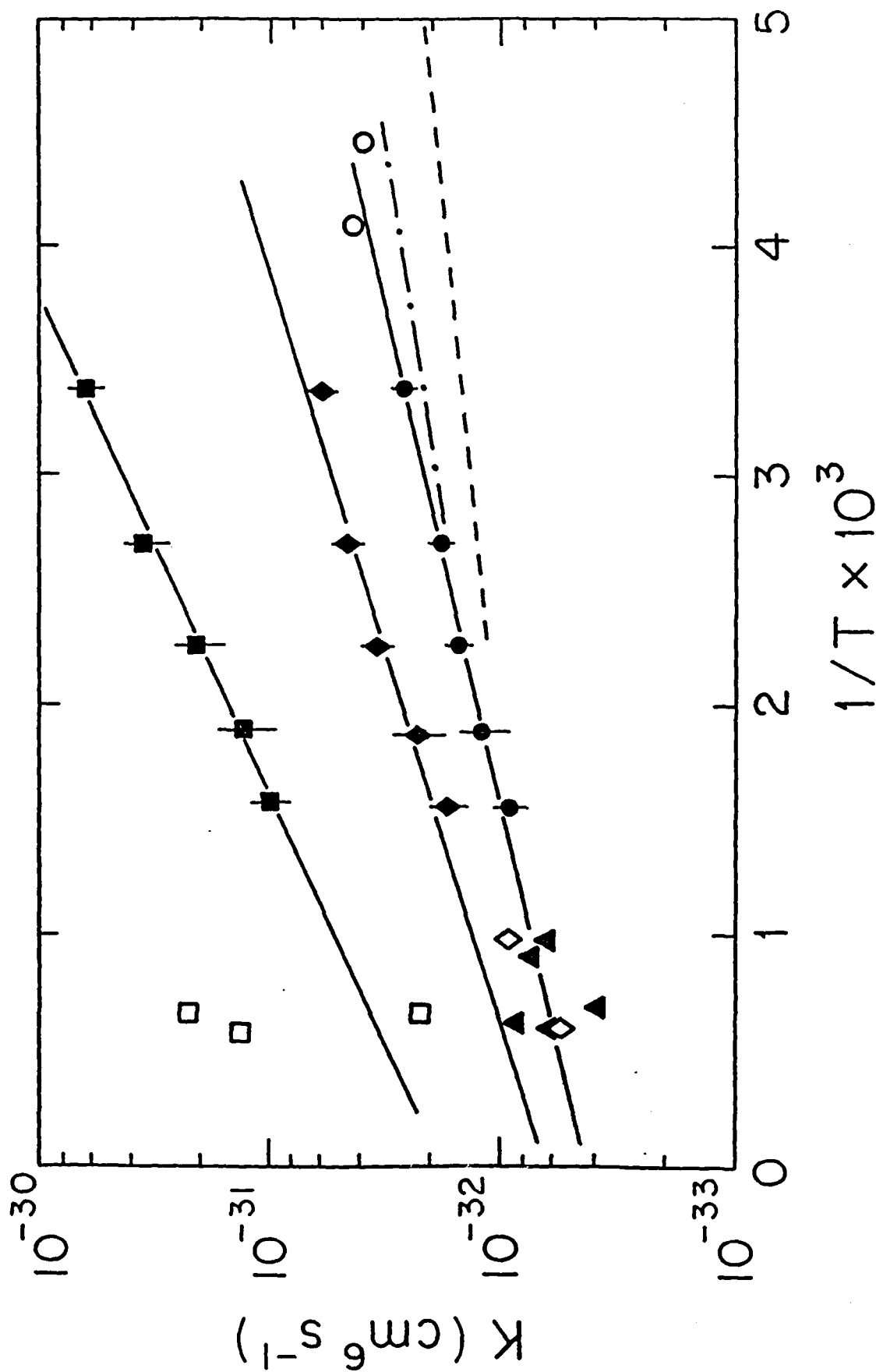


Figure 5. Arrhenius plot for H + O<sub>2</sub> + M third-order rate constants.  
Third body:  $\Delta$  Ar,  $\circ$  He,  $\diamond$  N<sub>2</sub>,  $\square$  H<sub>2</sub>O

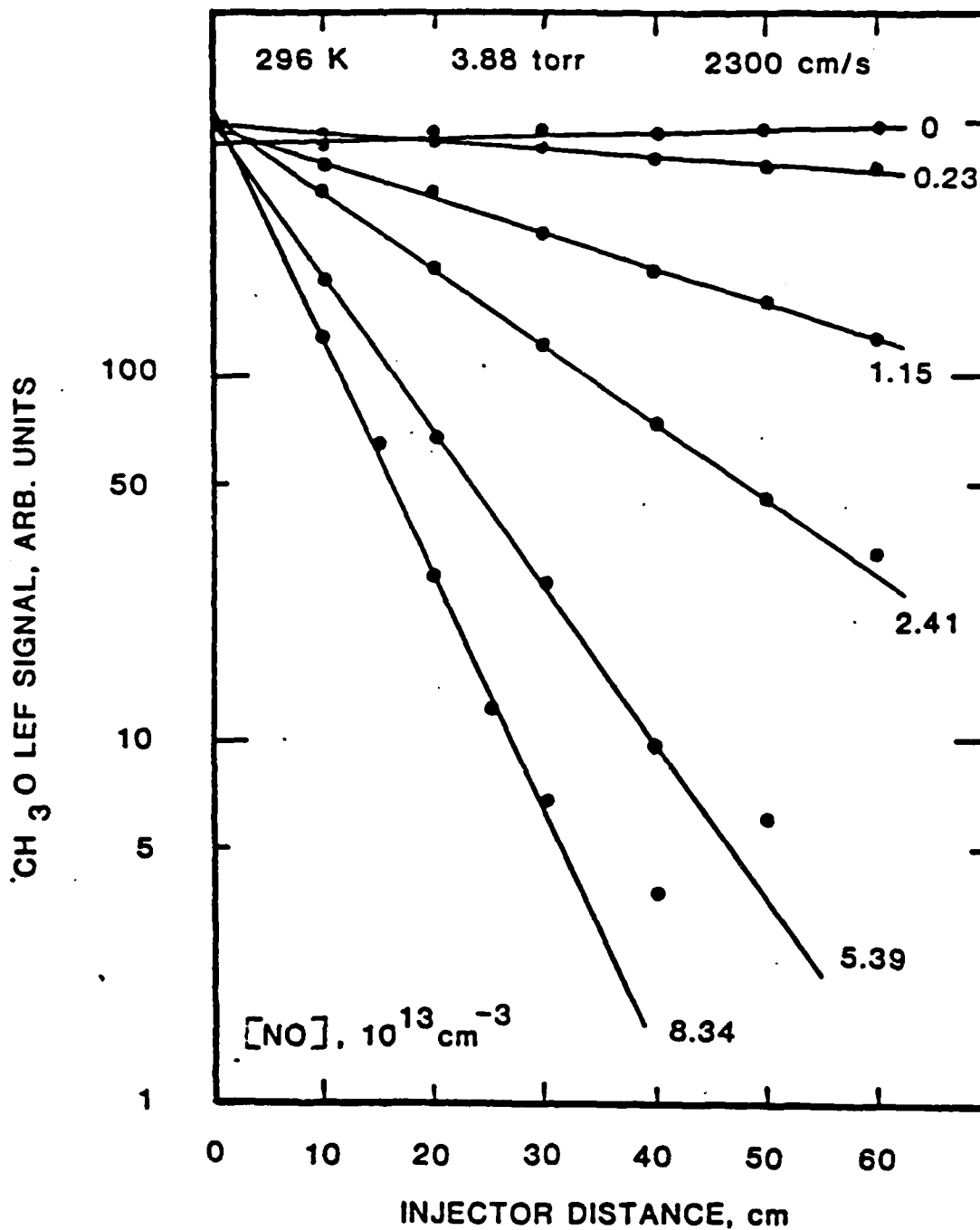


Figure 6. CH<sub>3</sub>O + NO: decay plots with curvature attributed to CH<sub>3</sub>O self-reaction

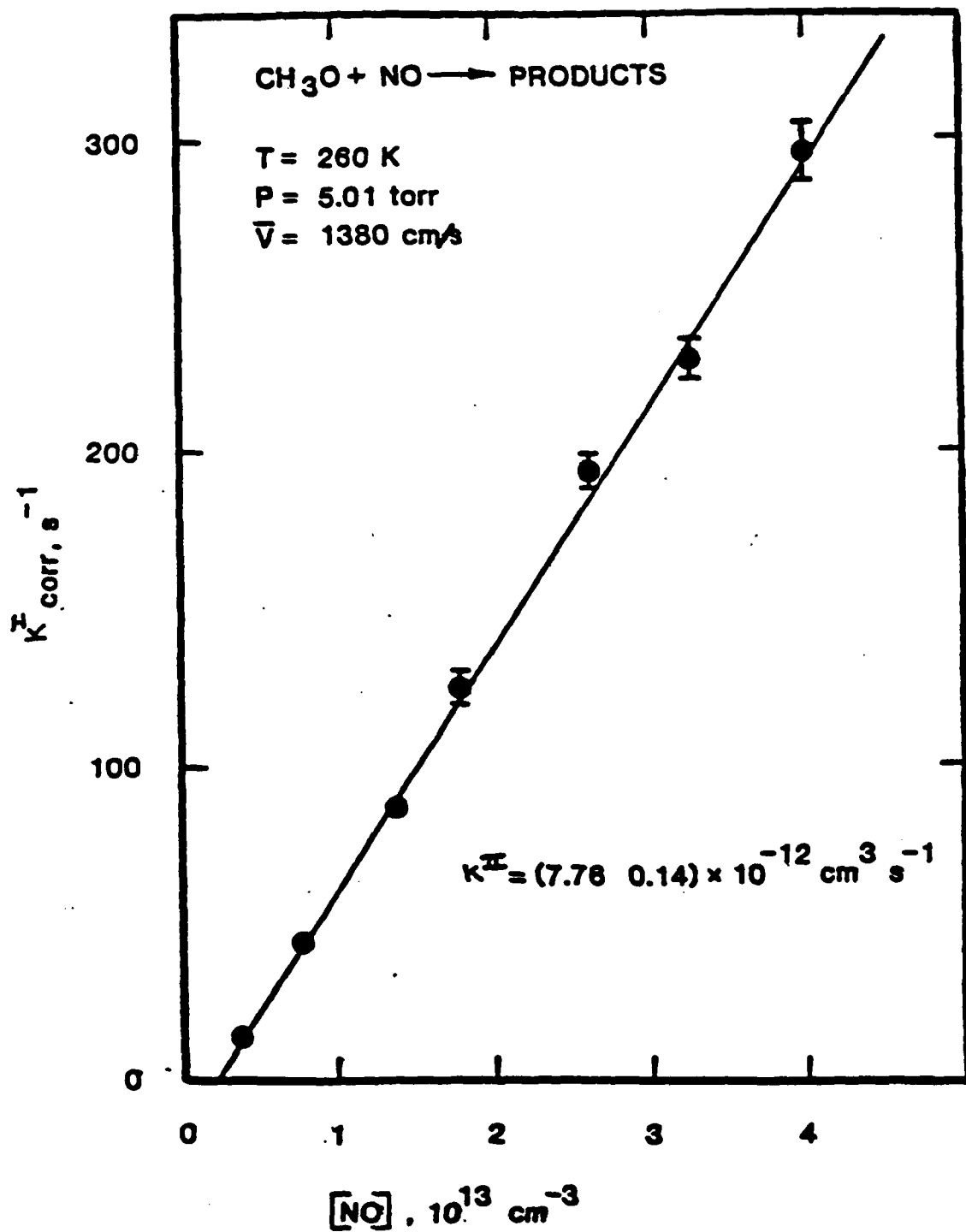


Figure 7. CH<sub>3</sub>O + NO:  $k^z_{\text{corr}}$  vs [NO]

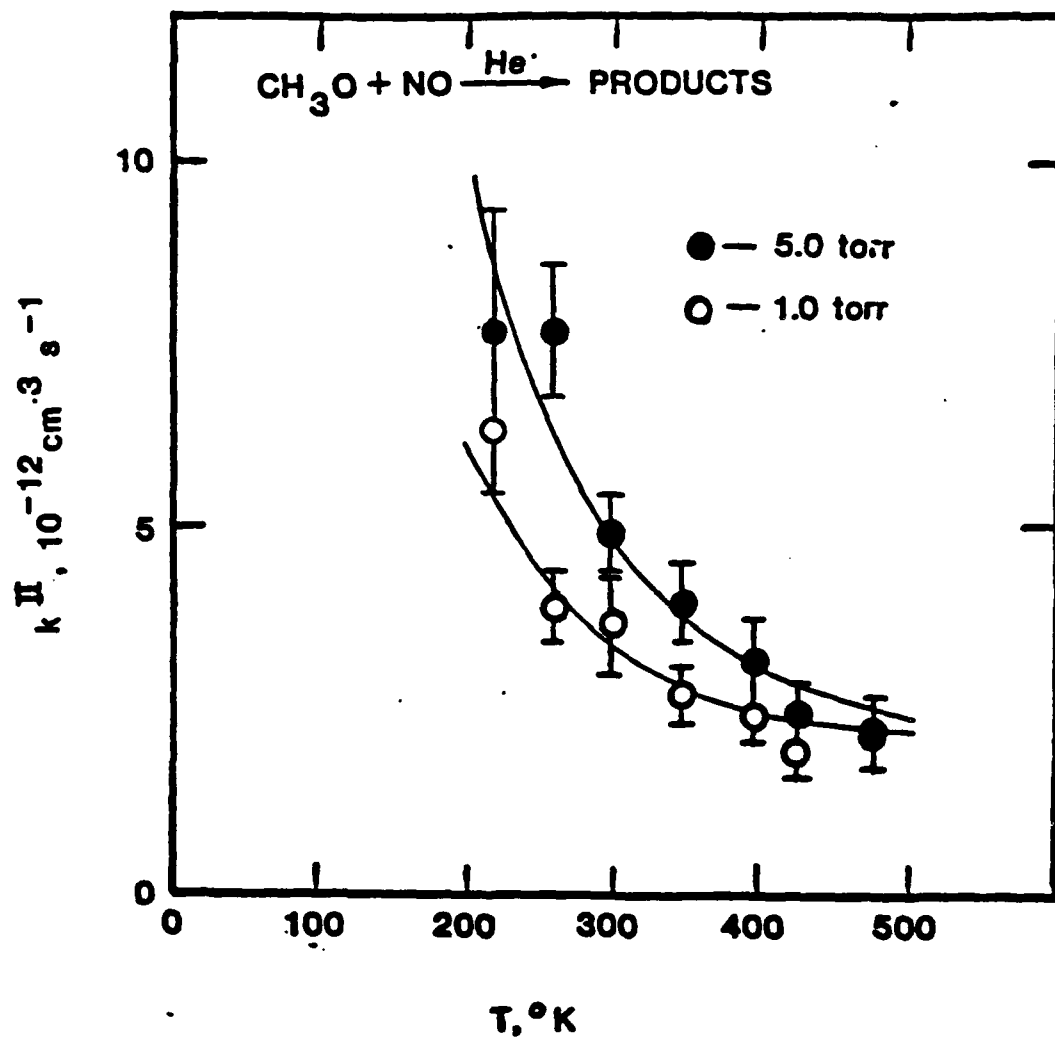


Figure 8.  $\text{CH}_3\text{O} + \text{NO}$ : pressure and temperature dependence of  $k_{II}$

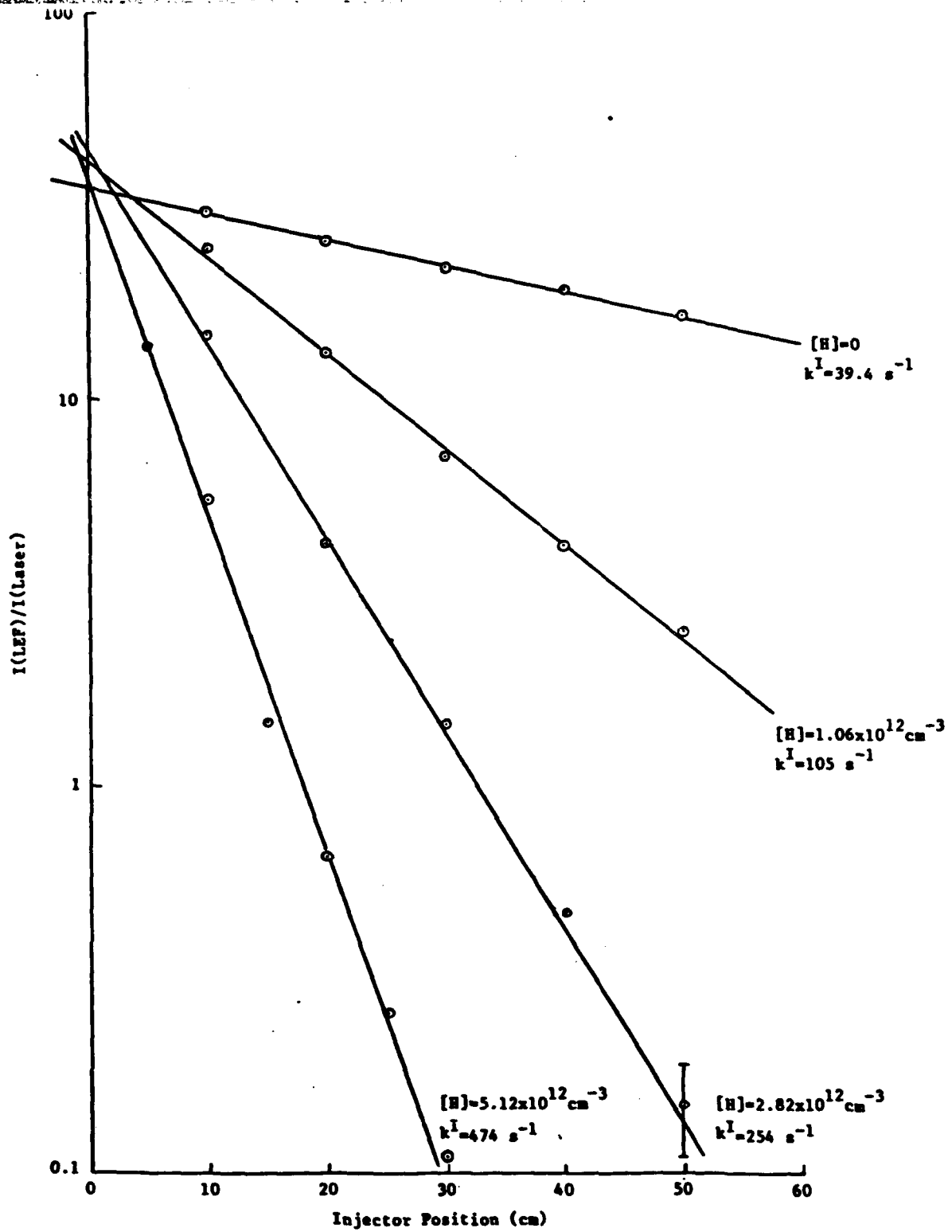


Figure 9.  $\text{CH}_3\text{O} + \text{H}$ : decay curves

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