and anions can overlap and be mutually destructive.<sup>14</sup> Thus, the hydration number of Na<sup>+</sup> from the present study is smaller than from MD, as expected. The broad maximum in the  $\alpha$  vs.  $n_w$  curve is also consistent with the above result that the second hydration shell of Na<sup>+</sup> is not well-defined, i.e. weakly formed. In the case of Cs<sup>+</sup>, MD results show that only a few molecules of the first hydration shell of Cs<sup>+</sup> are oriented and the rest are not.<sup>10</sup> This lack of orientational order in the water molecules of the first hydration shell has been interpreted as indicative of weak interactions among themselves and is consistent with the observation that  $\alpha_{CsR}$  ( $n_w \leq 3$ ) is greater than  $\alpha_{NaR}$  or  $\alpha_{KR}$  ( $n_w \leq 3$ ) and the hydration number is very much smaller than the reported values (Table III).

Dielectric permittivity measurements on aqueous electrolyte solutions give hydration numbers<sup>15</sup> as water molecules whose rotation is strongly hindered (generally referred to as "irrotationally" bound water molecules). Hydration numbers from such studies<sup>16,17</sup> (Table III) show good agreement with the ones reported here. This strongly supports the above interpretation of isotope effects in terms of strongly oriented and hydrogenbonded (to water molecules in the next layer) water molecules in the first hydration shell. The strength of the hydrogen bonds between first and second layer water molecules is governed by the polarization of H atoms of first layer water molecules by the cation. This polarization depends upon the ion-dipole interactions, whose strength is governed by the charge density on the cation.  $\alpha_{\rm max}$ , therefore, follows the same sequence as the charge density on cations, i.e.  $Li^+ > Na^+ > K^+ > Cs^+$ .

The significant results from the above discussion are (i) the second hydration shell around Na<sup>+</sup> and (ii) the behavior of K<sup>+</sup> as structure makers. In quantum-mechanical calculations of single ions and water molecules,<sup>18</sup> where interfering effects of anions are absent, the first and second hydration shells for Na<sup>+</sup> and K<sup>+</sup> have been found to be energetically stable. Similar behavior of Na<sup>+</sup> and K<sup>+</sup> in the resin phase suggests that the interfering effects of the anions are absent in the resin phase. This would imply that the interaction of the sulfonate groups with water molecules or

alkali metal cations is not as strong as water-water and cationwater interactions. Independent studies on the resin phase have shown that sulfonate groups are not hydrated in the resin phase<sup>19</sup> and there are no specific interactions of alkali metal cations and these ionogenic groups.<sup>20</sup> This emphasizes that the resin phase in alkali metal ion form resembles single ion solutions when cation-water and water-water interactions predominate.

In conclusion, the following picture of the hydration of alkali metal ions in the resin phase, or aqueous solutions, emerges. When small numbers of water molecules per cation are present, all the cations are able to orient and bind them. And there are no water-water interactions in the first hydration shell. In the case of CsR, the lack of orientational order in the first hydration shell leads to weak water-water interactions in it. The cation-water interaction decreases from Li<sup>+</sup> to Cs<sup>+</sup>. As such, hydration numbers also decrease in the same order. These oriented water molecules in the first hydration shell form hydrogen bonds with water molecules in the next layer. The strength of these hydrogen bonds is given by  $\alpha_{max}$  or more precisely by  $\alpha_2$ . Though stronger hydrogen bonds between first and second hydration shell water molecules have been predicted earlier also,<sup>21</sup> this study provides for the first time a quantitative measure of their strength. The strength of these hydrogen bonds decreases from Li<sup>+</sup> to Cs<sup>+</sup>---in agreement with the decreasing polarizing effect of the cations (in this series) on the water molecules of the first hydration shell. Due to hydrogen-bond formation with the water molecules of the next layer, the water molecules in the first hydration shell are rotationally hindered. Consequently, the hydration numbers from the present study are in agreement with those from dielectric permittivity measurements on aqueous electrolyte solutions, but are lower than those from X-ray, neutron diffraction, or molecular dynamics studies. The existence of the interfering effects of the anions on the hydration of cations in aqueous electrolyte solutions is strikingly demonstrated by the second hydration shell for sodium ions and the structure-making behavior of potassium ions in the resin phase. This emphasizes that the resin phase resembles single ion solutions. In the region of high water content, water-water interactions predominate (the influence of cations not extending beyond the second layer), though the hydrophobic interactions due to the resin network cannot be ruled out.

# High-Pressure Falloff Curves and Specific Rate Constants for the Reaction $CH_3 + O_2 \rightleftharpoons$ $CH_3O_2 \rightleftharpoons CH_3O + O$

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The recombination reaction  $CH_3 + O_2 \rightarrow CH_3O_2$  was studied at room temperature by laser flash photolysis over the pressure range 0.25-150 bar in the bath gases Ar and N<sub>2</sub>. Falloff curves are constructed, leading to a limiting high-pressure rate constant of  $k_{\text{rec},\infty} = (2.2 \pm 0.3) \times 10^{-12} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. By use of a simplified statistical adiabatic channel model, on the basis of the measured  $k_{rec,\infty}$  a set of specific rate constants k(E,J) is calculated for the unimolecular dissociation CH<sub>3</sub>O<sub>2</sub>  $\rightarrow$  CH<sub>3</sub> + O<sub>2</sub> and compared with the reaction CH<sub>3</sub>O<sub>2</sub>  $\rightarrow$  CH<sub>3</sub>O + O. With the derived specific rate constants, thermal rate constants for the reaction CH<sub>3</sub> + O<sub>2</sub>  $\Rightarrow$  CH<sub>3</sub>O + O are calculated and compared with experiments.

# Introduction

The reactions of alkyl radicals with molecular oxygen are key processes in hydrocarbon oxidation. Similarly as in the reaction

of hydrogen atoms with molecular oxygen, there is the possibility of addition or chain branching. The relative ratio of these pathways depends on temperature and pressure in a complicated fashion. Unimolecular rate theory permits the quantitative disentanglement of the competing reaction channels under various reaction conditions. In order to do this analysis, measurements

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Kinetics of  $CH_3 + O_2 \rightleftharpoons CH_3O_2 \rightleftharpoons CH_3O + O$ 



Figure 1. Schematic diagram of the apparatus.

of limiting rate constants at low and high pressures and low and high temperatures are required. In our laboratory we have measured a series of room-temperature falloff curves over a wide pressure range. For example, the addition reaction

$$H + O_2 (+M) \rightarrow HO_2 (+M)$$
(1)

was studied up to pressures of the bath gas M of 200 bar.<sup>1</sup> Modeling of this process in terms of unimolecular rate theory provided an access not only to specific rate constants of dissociation of excited  $HO_2^*$  into  $H + O_2$  or HO + O but also to the chain branching reaction

$$H + O_2 \rightarrow HO + O$$
 (2)

which apparently proceeds via the same HO<sub>2</sub>\* intermediate complex as reaction 1.

By analogy with reactions 1 and 2, in the present work we study the addition of methyl radicals to molecular oxygen

$$CH_3 + O_2 (+M) \rightarrow CH_3O_2 (+M)$$
(3)

We analyze our results again by unimolecular rate theory and compare with rate constants of the chain branching process

$$CH_3 + O_2 \rightarrow CH_3O + O \tag{4}$$

which is analogous to reaction 2. Different from the  $HO_2$  system, there is the possibility of the additional reactions

$$CH_3 + O_2 \rightarrow CH_2O + OH$$
 (5)

$$\rightarrow CH_2 + HO_2$$
 (6)

There has been an intense and still controversial discussion about the rates and relative importances of reactions 3-6 in hydrocarbon oxidation under high-temperature combustion and low-temperature atmospheric oxidation conditions.<sup>2-16</sup> Measurements<sup>2-7,10,11</sup> of

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the addition reaction 3, under conditions where it dominates over other pathways like reactions 4-6, so far were restricted to pressures below 1 bar. As a consequence, constructions of falloff curves were relatively uncertain. Our present measurements up to 200 bar eliminate this problem.

# **Experimental Section**

CH<sub>3</sub> radicals were produced by the laser photolysis of azomethane. The reactions of CH<sub>3</sub> radicals with molecular oxygen were followed by UV absorption of either the CH<sub>3</sub> radicals or the reaction product  $CH_3O_2$ . The reaction times were in the order of microseconds while CH<sub>3</sub> radicals were produced in 15 ns. Thus, there was a complete separation between production and subsequent reaction of methyl radicals.

A schematic diagram of the apparatus used in this investigation is shown in Figure 1. A detailed description of the high-pressure reactor was given elsewhere<sup>17,18</sup> and hence will not be repeated here. Briefly, a machined stainless steel block with an internal volume of about 20 cm<sup>3</sup> with four quartz windows (20 mm thick) served as the reactor. The photolysis and the probe beams intersected at the center of the cell where the reaction of interest was studied. The probe beam consisted of the collimated output of a continuous Xe-Hg high-pressure arc lamp (Hanovia Type 901B, 200 W) which traversed the reactor. This beam was dispersed by a monochromator (ZEISS M4 QIII), and light at the wavelengths of interest was detected by a photomultiplier (RCA 1P28). The output was amplified by a wide-band amplifier and digitized by a 100-MHz digital oscilloscope wave form analyzer (Gould-Biomation Model 4500). The photolysis beam was from an ArF excimer laser (Lambda Physik EMG 200, 10-ns pulses, 193 nm, up to 100 mJ/cm<sup>2</sup>) with a usable cross section area of  $1 \text{ cm}^2$  (0.5 cm × 2 cm). The probe beam intersected the photolysis beam along the 2-cm axis; thus, the path length for observation of kinetics was 2 cm. The fluence of the excimer laser entering the reactor was varied by using a quartz attenuator. The transmitted 193-nm beam energy was measured by a Gen Tec pyroelectric detector whose accuracy is estimated to be about 20%.

CH<sub>3</sub> radicals were produced via the laser-induced photolysis . . . .

$$CH_3 - N = N - CH_3 \rightarrow 2CH_3 + N_2$$
(7)

at a wavelength of 193 nm. Reaction 3 was studied under pseudo-first-order conditions in  $CH_3$  with the reactant  $O_2$  in large excess over CH<sub>3</sub> radicals. Experiments were performed with mixtures of 0.1-1 torr of azomethane, 0.25-150 bar of diluent gas ( $N_2$  or Ar), and 10–200 torr of  $O_2$ . The reactor was first filled with the mixture of azomethane and diluent nitrogen or argon; then, oxygen was added and was finally pressurized with the diluent gas. This procedure ensured complete mixing. All experiments were carried out under static conditions. The number of flashes applied to each mixture was varied to check for product formation. In many experiments, mixtures were irradiated with single shots. Up to 16 individual traces were then averaged to obtain good signal to noise ratios in the measured radical concentration profiles. The accuracy of pressure measurements for  $O_2$  was better than  $\pm 3\%$  while that for the total pressure was about  $\pm 5\%$  above 14 bar. Below 14 bar, the total pressure was known to better than  $\pm 3\%$ .

Reaction 3 was investigated by monitoring absorption signals at 240 nm (used spectral resolution  $\Delta\lambda(fwhm) = 3$  nm) where the  $CH_3O_2$  product absorbs. Also, the absorption at 216 nm  $(\Delta\lambda(fwhm) = 0.2 \text{ nm})$  due to CH<sub>3</sub> was recorded. With this choice

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Figure 2. Absorption-time profile of CH<sub>3</sub>O<sub>2</sub> formation (observation at 248 nm, [CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>]<sub>0</sub> =  $2.5 \times 10^{16}$  molecule cm<sup>-3</sup>, [O<sub>2</sub>] =  $1.5 \times 10^{18}$  molecule cm<sup>-3</sup>,  $P(N_2) = 0.7$  bar, laser energy = 3 mJ cm<sup>-2</sup>, T = 298 K).



Figure 3. Falloff curve for the recombination reaction  $CH_3 + O_2 + N_2 \rightarrow CH_3O_2 + N_2$  at 298 K: ( $\bullet$ ), experiments from this work; (O), experiments by Selzer and Bayes.<sup>11</sup> Data evaluations: (---), ref 15; (---), ref 16 and 24.

of wavelengths there were no interferences with the absorption of azomethane itself. Even though azomethane does absorb in this spectral range, its cross section<sup>19</sup> is at least 10<sup>3</sup> times smaller than that of  $CH_3^{20,21}$  and  $CH_3O_2^{.5.6}$  The absorption cross section for  $CH_3$  radicals at 240 nm is sufficiently small; thus, upon measurement of reaction 3 via  $CH_3O_2$  absorption,  $CH_3$  absorption did not interfere with the observations at 240 nm.

The reaction could be followed either by  $CH_3O_2$  formation or  $CH_3$  consumption. Both methods gave identical results. However, the majority of data were measured via  $CH_3O_2$  formation because the  $CH_3$  absorption coefficient decreases at high pressures.<sup>50</sup>

Azomethane was prepared according to the method given by Renaud and Leitch.<sup>22</sup> It was distilled from 197 to 77 K several times and the middle fraction retained for use. Azomethane was degassed several times, and mixtures of azomethane in the diluent gas were prepared manometrically. The azomethane mixture was stored in darkened bulbs to avoid photolysis. N<sub>2</sub>, O<sub>2</sub>, and Ar were from Messer-Griesheim with stated purities of 99.996%. They were used as supplied.

## Results

Reaction 3 under pseudo-first-order conditions was studied by monitoring the absorption of  $CH_3O_2$  at 240 nm. A typical time profile of  $CH_3O_2$  formation is shown in Figure 2. The digital oscilloscope was pretriggered such that the transmitted probe beam intensity in the absence of  $CH_3O_2$  could be measured. As seen in Figure 2, the absorption due to  $CH_3O_2$  increases after the laser flash and reaches a maximum. Furthermore, upon reaching the maximum, it stays constant for a long time.  $CH_3O_2$  decay is controlled by the self-reaction

$$CH_3O_2 + CH_3O_2 \rightarrow products$$
 (8)

which for our experimental monitoring times of less than 50  $\mu$ s is negligible<sup>15,16</sup> for the present concentrations of CH<sub>3</sub>O<sub>2</sub>. The analysis of the curve is straightforward since the absorbance was

TABLE I: Measured Rate Coefficients  $k_3$  for the Reaction CH<sub>3</sub> +  $O_2 + M \rightarrow CH_3O_2 + M$ 

М	P(M)/bar	P(O <sub>2</sub> )/torr	$k_3/10^{-12} \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>
N <sub>2</sub>		96	0.31
-	0.22	51	0.57
	0.27	30	0.76
	0.30	63	0.58
	0.44	39	0.97
	0.65	47	0.95
	0.68	46	0.96
	1.00	12	1.24
	1.00	22	1.08
	1.00	31	0.99
	2.0	31	1.28
	2.1	106	1.28
	2.1	141	1.24
	10	40	1.5
	10	70	1.9
	50	41	1.8
	100	50	1.7
Ar	0.22	45	0.54
	0.37	55	0.66
	1.07	95	0.90
	2.1	44	1.24
	148	79	1.60
	148	79	2.10

#### TABLE II: Secondary Reactions Influencing CH<sub>3</sub>O<sub>2</sub> Profiles<sup>a</sup>

	$k/\mathrm{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>
$CH_3 + O_2 \rightarrow CH_3O_2$	в
$CH_3 + CH_3 \rightarrow C_2H_6$	$4.8 \times 10^{-11}$
$CH_3 + CH_3O_2 \rightarrow 2CH_3O$	$6.0 \times 10^{-11}$
$CH_3 + CH_3O \rightarrow CH_4 + CH_2O$	$4.0 \times 10^{-11}$
$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O$	$2.2 \times 10^{-11}$
$CH_3O + CH_3O_2 \rightarrow CH_3OOH + CH_2O$	$1.3 \times 10^{-11}$
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$	$2.3 \times 10^{-13}$
$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	$1.0 \times 10^{-13}$

<sup>a</sup>Rate constants used for simulations; see text. <sup>b</sup>Figures 3 and 4.



Figure 4. Falloff curve for the recombination reaction  $CH_3 + O_2 + Ar \rightarrow CH_3O_2 + Ar$  at 298 K: ( $\bullet$ ), experiments from this work; ( $\Delta$ ), experiments by Smith and Pilling;<sup>13</sup> (O), experiments by Selzer and Bayes.<sup>11</sup>

always kept at values smaller than 4% such that the absorbance was proportional to [CH<sub>3</sub>O<sub>2</sub>]. The CH<sub>3</sub>O<sub>2</sub> formation followed first-order rate laws

$$[CH_{3}O_{2}] = [CH_{3}O_{2}]_{max}\{1 - \exp(-k_{3}[O_{2}]t)\}$$
(9)

with  $k_3[O_2]$  in our study varying between  $0.5 \times 10^6$  and  $3.5 \times 10^6$  s<sup>-1</sup> depending on the pressure of diluent and the concentration of O<sub>2</sub>.  $k_3[O_2]$  was always maintained in this range by varying  $[O_2]$ , in order to avoid secondary reactions. At each pressure we checked for total conversion of methyl radicals into CH<sub>3</sub>O<sub>2</sub>. The  $k_3$  values obtained for nitrogen and argon as diluent gases are summarized in Table I and illustrated in Figures 3 and 4. The overall accuracy of the measurements is estimated to be about  $\pm 15\%$  and is mostly controlled by the accuracy of evaluation of the absorption-time profiles.

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In order to be sure that no side processes were disturbing our measurements, at first we did a series of experimental tests. We varied  $O_2$  between 10 and 150 torr at constant azomethane pressure and laser energy. Initial methyl concentrations varied between 0.01 and 0.1 torr. The final CH<sub>3</sub>O<sub>2</sub> yield was found to be constant (within  $\pm 15\%$ ). All experiments were carried out using ratios of  $[O_2]/[CH_3O_2]$  in the range 350-1500. The measured  $k_3$  was also found to be independent of the azomethane concentration. A numerical simulation of the reaction system including methyl recombination, methyl attack on CH<sub>3</sub>O<sub>2</sub> forming methoxy radicals, reactions of methoxy, and other processes did confirm our conclusion that no disturbance by side processes interfered. Table II shows the reactions and rate parameters employed in our simulations.

If O<sub>2</sub> had also been photolyzed in our experiments, two complications would have occurred: (i)  $O(^{3}P)$  atoms produced could have reacted with CH<sub>3</sub> or CH<sub>3</sub>O<sub>2</sub> radicals, and (ii) O(<sup>3</sup>P) would have added to  $O_2$  to form ozone which absorbs at 240 nm. The ArF excimer laser has a line width of a few angstroms.  $O_2$ absorption<sup>23</sup> at 193 nm is very structured, with peak to valley cross section ratios of over 40 and a cross section of about  $4 \times 10^{-23}$ cm<sup>2</sup> at the valley. Since the 193-nm photolysis beam traveled through 1 m of room air before entering the reactor, the pulse was selectively filtered to remove those wavelengths that can photolyze  $O_2$ . Even if this filtering effect were absent, with 100 torr of  $O_2$  in the cell and with the usual laser fluences that were used (10 mJ cm<sup>-2</sup>) only 0.3 mtorr of oxygen atoms was produced. This concentration is about 100 times lower than that of methyl radicals produced by the photolysis of azomethane and hence would not have caused any chemical complications. All  $O(^{3}P)$ would most likely react with O2 to form O3. However, 0.3 mtorr of O3 cannot contribute significantly to the measured signal at 240 nm. To check for this, a mixture of 150 torr of  $O_2$  in 2 atm of  $N_2$  was photolyzed by using laser pulses of 40 mJ cm<sup>-2</sup>. No observable signal was detected. Therefore, O<sub>2</sub> photolysis did not affect the measured values of  $k_3$ .

#### Discussion

Comparison with Previous Measurements. The combination of methyl radicals with O<sub>2</sub> has been previously investigated by using kinetic spectroscopy techniques<sup>2,3,5</sup> (i.e., pulsed photolysis to generate CH<sub>3</sub> radicals and 216-nm absorption for its detection), molecular modulation methods,<sup>6</sup> and photolysis followed by end product analysis.<sup>4</sup> Measurements prior to 1970 have been summarized in the paper by Basco et al.<sup>2</sup> Since none of these earlier studies has measured  $k_3$  at pressures greater than 1 bar and since in all but one study  $k_3$  increases monotonically up to the highest employed pressures, the value of  $k_{3,\infty}$  was obtained by extrapolation. Basco et al.<sup>2</sup> were the only ones to see  $k_1$  reach a "highpressure limit". However, their results are in disagreement with those of all other investigators including van den Bergh and Callear,3 who employed an almost identical experimental procedure. In a recent paper, Smith and Pilling<sup>13</sup> studied the same reaction in the pressure range 30-500 torr of Ar using the same technique as applied in our work. Their values are in good agreement with our own results (see Figure 4) although they lead to a slightly lower value of  $k_{3,\infty}$ . Smith and Pilling propose that higher reaction rates measured earlier were due to secondary reactions present in the case of too high initial ratios  $[CH_3]_0/[O_2]$ . Our simulations using the mechanism of Table II confirm this suggestion: One finds an increase of the apparent reaction rate for methyl decay or for CH<sub>3</sub>O<sub>2</sub> formation at high initial  $[CH_3]_0/[O_2]$ . At low pressures (0.5-6 torr), Selzer and Bayes<sup>11</sup> studied reaction 3 using laser flash photolysis of nitromethane together with photoionization detection of methyl radicals. In Figures 3 and 4 we show our results together with the results from Smith and Pilling and from Selzer and Bayes. We also show falloff curves constructed through these points for the two different diluents Ar and N<sub>2</sub> (see below). These results all fit together very

well. They clearly show that, at pressures below 10 bar of  $N_2$ or Ar, reaction 3 is still in the falloff regime. Even at highest pressures applied (about 150 bar), the second-order limiting high-pressure rate coefficient is approached only to within 20%. Similarly, at low pressures (0.5 torr of Ar) the experimental points are about 30% below the third-order limiting low-pressure rate coefficient.

The limiting low-pressure rate coefficients obtained from the falloff curves in Figures 3 and 4 are

$$k_{3,0} = [Ar](7.0 \pm 1.0) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
 (10)

 $k_{3,0} = [N_2](8.0 \pm 1.0) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (11)

for the bath gases Ar and  $N_2$ , respectively. For both gases the same limiting high-pressure rate coefficient of

$$k_{3,\infty} = (2.2 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (12)

was determined. These results have been included in the last CODATA compilation.<sup>24</sup> The given error limits are based on the scatter of data and on the estimate of possible systematic errors such as uncertainties in the falloff curves.

For the construction of the falloff curves it is necessary to analyze the experiments in terms of unimolecular rate theory. In practice this analysis involves a preliminary construction of reduced falloff curves, an extrapolation of the measured rate coefficients with these falloff curves toward the limiting low- and high-pressure rate coefficients, a theoretical interpretation of the limiting rate coefficients leading to a refined construction of the falloff curves, and a final fit. This procedure has been described in detail earlier<sup>1</sup> and was also applied in the present work. In the following we give an interpretation of our final results.

Limiting High-Pressure Rate Coefficient. We interpret the derived  $k_{3,\infty}$  value in terms of the simplified version of the adiabatic channel model, which was proposed in its canonical form in ref 25 and in its microcanonical form in ref 26. According to ref 25 one has

$$k_{3,\infty} = \frac{1}{K_{\rm c}} \frac{kT}{h} \frac{Q^*_{\rm cent} F^*_{\rm AM} \Pi Q^*_j \Pi Q^*_m}{\sigma^* Q_{\rm vib} Q_{\rm rot}} \exp\left(\frac{\Delta H_0^\circ + \Delta E_{\rm oz}}{kT}\right)$$
(13)

In this equation  $K_c$  denotes the equilibrium constant  $([CH_3][O_2]/[CH_3O_2])_{eq}$  of reaction 3,  $\hat{Q}^*_{cent}$  the centrifugal pseudopartition function,  $F^*_{AM}$  an angular momentum coupling correction factor,  $\sigma^*$  an effective symmetry number,  $\prod' Q^*$ , the pseudopartition function of the r conserved oscillators of  $CH_3O_2$ , and  $\prod^{b}Q^{*}_{m}$  the pseudopartition function of the b disappearing oscillators of  $CH_3O_2$  transforming into product rotors.  $Q_{vib}$  and  $Q_{\rm rot}$  are vibrational and rotational partition functions of CH<sub>3</sub>O<sub>2</sub>,  $\Delta H_0^{\circ}$  is the reaction enthalpy at 0 K, and  $\Delta E_{oz}$  is the energy barrier of the lowest adiabatic reaction channel for combination which arises from the change in the zero-point energies between reactant and products. With the relationships from ref 25, the factors in eq 12 are easily calculated as a function of the ratio  $\alpha/\beta$  between the looseness parameter  $\alpha$  and the Morse parameter  $\beta$ . The molecular parameters necessary for the calculation are given in the Appendix. With the fitted value

$$\alpha = 1.10 \text{ Å}^{-1} \tag{14}$$

and the calculated  $\beta = 3.37 \text{ Å}^{-1}$  (by using the 960-cm<sup>-1</sup> oscillator corresponding to the stretching of the C-O bond for the reaction coordinate; see Appendix), the experimental value of  $k_{3,\infty} = 2.2$ ×  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is reproduced. It should be emphasized that the Boltzmann factor  $\exp(-\Delta H_0^{\circ}/kT)$  and molecular partition functions  $Q_{vib}Q_{rot}$  contained in  $K_c$  cancel in eq 12. The result,

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therefore, depends on uncertainties in  $\Delta H_0^{\circ}$  only to a minor extent.

The derived looseness parameter  $\alpha = 1.10 \text{ Å}^{-1}$  of the CH<sub>3</sub>O<sub>2</sub> potential energy surface (uncertainty of  $\pm 10\%$ ) is very close to the "standard value"  $\alpha = 1.0 \text{ Å}^{-1}$  often observed<sup>27-29</sup> in reactions of this type. It is also very close to the value  $\alpha = 0.94$  Å<sup>-1</sup> observed<sup>1</sup> in the addition  $H + O_2 \rightarrow HO_2$  (1). Once the  $\alpha$  value is fixed by a fit to one experimental quantity, other quantities can be predicted. In particular, the temperature dependence of  $k_{3,\infty}$ over the range 200-400 K is calculated by using eq 12 to be

$$k_{3\infty} = 2.2 \times 10^{-12} (T/300 \text{ K})^{0.94} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (15)

At higher temperatures, the temperature coefficient becomes smaller. For 1500 K, a value of  $k_{3,\infty} = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$  $s^{-1}$  is calculated.

Limiting Low-Pressure Rate Coefficients. The derived  $k_{3,0}$ values are analyzed in terms of the expression from ref 30-32  $k_{10} =$ 

$$\frac{[\mathbf{M}]}{K_{\rm c}}\beta_{\rm c}Z_{\rm LJ}\frac{\rho(E_0)kT}{Q_{\rm vib}}\exp\left(-\frac{\Delta H_0^{\rm o}+\Delta E_{\rm oz}}{kT}\right)F_{\rm anb}F_{\rm E}F_{\rm rot}F_{\rm rot\,int}$$
(16)

where  $\beta_c$  denotes the collision efficiency,  $Z_{LJ}$  is the Lennard-Jones collision frequency, and  $\rho(E_0)$  is the harmonic vibrational density of states at  $E_0$ ;  $F_E$  accounts for the energy dependence of the density of states,  $F_{anh}$  for anharmonicity,  $F_{rot}$  for rotational contributions, and  $F_{\rm rot\,int}$  for hindered internal rotations.  $Q_{\rm vib}$  and  $\exp(-\Delta H_0^{\circ}/kT)$  cancel against the corresponding terms in  $K_c$  (see above). The equilibrium constant  $K_c$  for reaction 3, calculated with the molecular constants given in the Appendix, are in good agreement with the recently measured values.<sup>33</sup> Since the  $K_c$ values do not enter our calculations, they are not given explicitly. In order to calculate the rotational factor  $F_{\rm rot}$ , it is important to employ a realistic radial dependence of the CH<sub>3</sub>-O<sub>2</sub> potential and an adequate centrifugal potential. The most simple van der Waals expression combined with a quasi-diatomic centrifugal potential<sup>31</sup> leads to  $F_{rot}(298 \text{ K}) = 10.9$  whereas a more realistic Morse interaction potential together with a triatomic centrifugal potential<sup>32</sup> leads to  $F_{rot}(298 \text{ K}) = 7.2$ . The latter approach was chosen here. The reaction has an appreciable adiabatic zero-point energy barrier,  $\Delta E_{oz} = 1.1 \text{ kJ mol}^{-1}$  which has to be taken into account. The value  $V_0 = 4.2 \text{ kJ mol}^{-1}$  was employed for the barrier for the internal rotation in  $F_{\rm rot\,int}$ .<sup>33</sup> By comparison of the strong collision rate coefficient ( $\beta_c = 1$ ) with the experimental values of  $k_{3,0}$ , the following values of the collision efficiencies  $\beta_c$  are derived:  $\dot{\beta}_c(Ar)$ = 0.12 and  $\beta_c(N_2)$  = 0.12. These experimental values, via the relationship<sup>30</sup>

$$\beta_{\rm c}/(1-\beta_{\rm c}^{1/2}) = -\langle \Delta E \rangle / F_{\rm E} kT \tag{17}$$

allow to obtain average energies  $\langle \Delta E \rangle$  transferred per collision. One derives in this way  $-\langle \Delta E \rangle = 0.5$  kJ mol<sup>-1</sup> for both bath gases. It should be emphasized that the uncertainties of the experiments and the theoretical analysis leave an uncertainty of probably a factor of 2 in these  $\langle \Delta E \rangle$  values. However, the order of magnitude agrees very well with the data for related systems<sup>31</sup> and with recent direct measurements in highly excited  $CS_2^{34}$  and  $SO_2^{35}$  molecules. It should be mentioned that the present calculation of  $k_{3,0}$  differs from that of ref 46 by about a factor of 4, since a better approximation for  $F_{\rm rot}$  was employed and the large adiabatic zeropoint barrier  $\Delta E_{oz}$  was taken into account as well as a hindered rotor correction.

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Equations 15 and 16 also allow to analyze the temperature coefficient of  $k_{3,0}$ . Over the range 200-400 K the following expressions were derived:

$$k_{3,0} =$$
  
[Ar](7.0 ± 1.0) × 10<sup>-31</sup>(T/300 K)<sup>-3.0</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>  
(18)

$$k_{3,0} =$$

$$[N_2](8.0 \pm 1.0) \times 10^{-31} (T/300 \text{ K})^{-3.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
(19)

if one assumes  $\langle \Delta E \rangle$  values independent of the temperature. A value of  $\langle \Delta E \rangle$  proportional to the temperature would lead to a low-pressure limiting rate coefficient  $k_{3,0}$  proportional to  $T^{-2.1}$ .

Falloff Curves. Following the concepts of ref 32, 36, and 37, the transition of  $k_3$  from  $k_{3,0}$  to  $k_{3,\infty}$  is represented by reduced falloff curves

$$\frac{k_3}{k_{3,\infty}} = \left(\frac{k_{3,0}/k_{3,\infty}}{1+k_{3,0}/k_{3,\infty}}\right) F^{\text{SC}}(k_{3,0}/k_{3,\infty}) F^{\text{WC}}(k_{3,0}/k_{3,\infty}) \quad (20)$$

The strong collision broadening factor  $F^{SC}$ , depending on the "reduced density scale"  $k_{3,0}/k_{3,\infty}$ , is expressed by the empirical relationships from ref 32 and 36 which were derived from rigid **RRKM** theory. These relations use the parameters  $S_{\rm K}$  and  $B_{\rm K}$ 

$$S_{\rm K} = 1 - \frac{1}{T} \frac{{\rm d} \ln Q^*}{{\rm d}(1/T)}$$
 (21)

$$B_{\rm K} = \left(\frac{S_{\rm K} - 1}{s - 1}\right) \left(\frac{E_0 + a(E_0)E_z}{kT}\right) \tag{22}$$

where the "activated complex partition function"  $Q^*$  is obtained from the formal expression for the limiting high-pressure rate coefficient

$$k_{3,\infty} = \frac{1}{K_{\rm c}} \frac{kT}{h} \frac{Q^*}{Q_{\rm vib}Q_{\rm rot}} \exp\left(-\frac{E_0}{kT}\right)$$
(23)

s is the number of oscillators for the newly formed molecule,  $E_z$ its zero-point energy,  $E_0$  its dissociation energy at 0 K, and  $a(E_0)$ the Whitten-Rabinovitch correction factor. The parameter  $S_K$ was determined by identifying expression 19 with eq 12 and 14, accounting in this way for rotational effects. By this procedure,  $S_{\rm K}$  = 5.6 and  $B_{\rm K}$  = 36.9 were obtained at 298 K. Besides the strong collision broadening factor  $F^{SC}$ , the weak collision broadening factors from ref 32 and 37 were calculated. Our final reduced falloff curves for M = Ar and  $N_2$  at 298 K can be expressed by

$$\log F^{\rm SC} F^{\rm WC} = \{1 + [\log (k_{3,0}/k_{3,\infty})/N]^2\}^{-1} \log F_{\rm cent}$$
(24)

with  $F_{cent} = 0.27$  and N = 1.47. Due to the inclusion of rotational and losseness effects in  $Q^*$ , the calculated  $F_{cent}$  is nearly a factor of 2 smaller than calculated in ref 46.

Specific Rate Constants k(E,J) for the Dissociation  $CH_3O_2$  $\rightarrow CH_3 + O_2$ . The looseness parameter  $\alpha$  of the CH<sub>3</sub>O<sub>2</sub> potential energy surface at the side of the  $CH_3 + O_2$  products has been fixed by comparing calculated  $k_{3,\infty}$  values from eq 12 with the experimentally obtained rate constant. Using this  $\alpha$  value, we have employed the microcanonical version of the simplified adiabatic channel model of ref 26 to construct a set of specific rate constants k(E,J) for dissociation of excited CH<sub>3</sub>O<sub>2</sub> radicals into CH<sub>3</sub> + O<sub>2</sub> fragments. Figure 5 shows the corresponding statistically calculated specific rate constants for angular momentum quantum numbers J = 0, 30, and 60 based on the  $\alpha$  value of 1.1 Å<sup>-1</sup>. One notices the same general features as observed and explained in earlier calculations of k(E,J) for NO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>,<sup>26,27</sup> H<sub>2</sub>CO, D<sub>2</sub>CO,<sup>38</sup>

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<b>FABLE III:</b> Comparison of	'Experimental a	nd Calculated	'Rate	Constants of	the Ro	eaction
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	$k_{-4}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$						
	calcd		exptl				
T/K	$\alpha = 1.0 \text{ Å}^{-1}$	$\alpha = 1.1 \text{ Å}^{-1}$	ref 39	ref 12	ref 40	ref 11	$K_4 = k_4/k_{-4}$
300	1.3	1.7				-	
800	1.8	2.2					
1150	2.2	2.6	1.5		0.94	0.57	$1.56 \times 10^{-5}$
1300	2.2	2.6	1.6		0.94	0.56	6.69 × 10 <sup>-5</sup>
1550	2.4	2.9	1.8		0.92	0.54	$4.14 \times 10^{-4}$
1800	2.6	3.0		0.57		0.52	$1.58 \times 10^{-3}$
2300	2.8	3.2		0.41		0.46	$1.03 \times 10^{-2}$

k.

"Calculations by simplified statistical adiabatic channel model.<sup>25</sup>



Figure 5. Specific rate constants k(E,J) for the dissociation reaction of  $CH_3O_2 \rightarrow CH_3 + O_2$ . Calculations by simplified statistical adiabatic channel model<sup>26</sup> with  $\alpha = 1.10$  Å<sup>-1</sup> for J = 0 ( $\blacktriangle$ ), J = 30 ( $\bigcirc$ ), and J = 60 ( $\bigcirc$ ).

and HO<sub>2</sub>.<sup>1</sup> At energies close to the dissociation threshold, k(E,J) decreases with increasing J, while at higher energies the curves for different J values merge and finally cross. In order to check our calculations for consistency, we have calculated the thermal rate constants by averaging our k(E,J) values over a thermal distribution. The result at 298 K of  $k_{3,\infty} = 2.1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is in agreement with the experimental value of 2.2  $\times 10^{-12}$  cm<sup>-3</sup> molecule<sup>-1</sup> s<sup>-1</sup> which has been used for the determination of the looseness parameter  $\alpha$ .

A comparison of the limiting high-pressure rate constants  $k_{3,\infty}$ and the specific rate constants k(E,J) for the dissociation CH<sub>3</sub>O<sub>2</sub>  $\rightarrow$  CH<sub>3</sub> + O<sub>2</sub> with the corresponding results for the system HO<sub>2</sub>  $\rightarrow$  H + O<sub>2</sub> is most interesting. Whereas  $k_{3,\infty} = 2.2 \times 10^{-12} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> has a comparably small value, for  $H + O_2 \rightarrow HO_2$ a value of  $7.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was measured.<sup>1</sup> Our analysis in terms of eq 12 allows to explain this difference. At first, in spite of the factor of 35 difference in  $k_{\infty}$ , there is a striking agreement in the looseness character of the potential surfaces such as expressed by nearly identical  $\alpha$  parameters ( $\alpha = 1.10 \text{ Å}^{-1}$  for  $CH_3O_2$ ,  $\alpha = 0.94 \text{ Å}^{-1}$  for HO<sub>2</sub>). It is, therefore, in the other better known molecular parameters and their respective influence on the various factors in  $k_{\infty}$  in eq 12, where the origin of the difference has to be found. The detailed analysis in ref 29 of the various factors contributing to  $k_{\text{rec},\infty}$  in reactions 1 and 3 clearly shows the differences: The "rigidity factors"  $f_{\text{rec},\infty}^{\text{rigid}} = F^*{}_{AM}\Pi Q^*{}_{J}\Pi Q^*{}_{m}$  $\exp(-\Delta E_{oz}/kT)/(\sigma^*Q_{\text{vib rot}}(B)Q_{\text{vib rot}}(C))$  of the recombination B + C  $\rightarrow$  A for A = CH<sub>3</sub>O<sub>2</sub> are 5 times smaller than for A = HO<sub>2</sub>, due to the larger number of disappearing oscillators. On the other hand, the "loose rate constants"  $k_{\rm rec,\infty}^{\rm loose} = (kT/h)(h^2/k^2)$  $2\pi\mu kT$ <sup>3/2</sup> $Q^*_{cent}(Q_{el}(A)/Q_{el}(B)Q_{el}(C))$  are 7 times smaller in part due to the 10 times smaller reduced mass  $\mu$ . The result is an about 35 times higher value of  $k_{\rm rec,\infty}$  in the HO<sub>2</sub> system compared to



Figure 6. Specific rate constants k(E,J) for the dissociation reaction of  $CH_3O_2 \rightarrow CH_3O + O$ . Calculations by simplified statistical adiabatic channel model<sup>26</sup> with  $\alpha = 1.0$  Å<sup>-1</sup> for J = 0 ( $\blacktriangle$ ), J = 60 ( $\bigcirc$ ), and J = 120 ( $\bigcirc$ ).

CH<sub>3</sub>O<sub>2</sub>, in spite of the fact that both systems appear to have identical ratios  $\alpha/\beta = 0.33$  of the looseness parameter  $\alpha$  and the Morse parameters  $\beta$  of the potential energy surface.<sup>29</sup> For more details the reader is referred to ref 29.

Specific Rate Constants k(E,J) for the Dissociation  $CH_3O_2$  $\rightarrow$  CH<sub>3</sub> + O and Thermal Rate Constants for the Reaction CH<sub>3</sub>  $+ O_2 \rightarrow CH_3O + O$ . In the HO<sub>2</sub> system, the H + O<sub>2</sub> and HO + O dissociation channels have quite different characters of the J dependence of the specific rate constants k(E,J). Whereas the  $H + O_2$  channel looks similar to Figure 5 although the individual values are more than 2 orders of magnitude larger than for CH<sub>3</sub>  $+ O_2$ , the HO + O channel behaves as a quasi-diatomic system without crossing of the various J curves. This tempted us to do an analogous calculation for the dissociation channel  $CH_3O_2 \rightarrow$  $CH_3O + O$ . There is no immediate reason for the looseness  $\alpha$ parameter at the  $CH_3O + O$  exit of the  $CH_3O_2$  potential surface to be the same as at the  $CH_3 + O_2$  exit. However, in the  $HO_2$ system the standard value  $\alpha = 1$  Å<sup>-1</sup> at the HO + O exit, being close to the derived value  $\alpha = 0.94 \text{ Å}^{-1}$  at the H + O<sub>2</sub> exit, resulted in very realistic predictions about the reaction H +  $O_2 \rightarrow HO$ + O. For this reason, we also use  $\alpha = 1 \text{ Å}^{-1}$  for the CH<sub>3</sub>O<sub>2</sub>  $\rightarrow$  $CH_3O + O$  channel in our present work. Our results are shown in Figure 6. Apart from the shift on the energy scale due to different threshold energies  $E_0(J=0)$ , we find that k(E,J) for the  $CH_3O + O$  channel is always at least a factor of 100 smaller than for the  $CH_3 + O_2$  channel. Since this factor is already present at the threshold rate constants  $k(E=E_0(J),J)$ , the difference obviously has to be due to different densities of states  $\rho(E,J)$  because of different dissociation energies. Apart from this, the variations of the k(E,J) curves with J are similar in character for the two channels. This confirms our interpretation of the differences in k(E,J) character in the HO<sub>2</sub> system, i.e. quasi-diatomic rotational character for the HO + O channel due to the light mass of H and polyatomic character for the channel  $H + O_2$  similar as for

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the two dissociation channels in CH<sub>3</sub>O<sub>2</sub>.

The fact of a much larger k(E,J) for  $CH_3O_2 \rightarrow CH_3 + O_2$ compared to  $CH_3O_2 \rightarrow CH_3O + O$  implies that the reaction  $CH_3O + O \rightarrow CH_3O_2^* \rightarrow CH_3 + O_2$  proceeds without any appreciable redissociation of  $CH_3O_2^*$ . Therefore, by analogy with the HO + O  $\rightarrow$  HO<sub>2</sub>\*  $\rightarrow$  H + O<sub>2</sub> reaction, the rate constant of the reaction  $CH_3O + O \rightarrow CH_3 + O_2$  should be identical with the high-pressure recombination rate coefficient for  $CH_3O + O$  $\rightarrow$  CH<sub>3</sub>O<sub>2</sub>. The latter follows directly by thermal averaging of our results in Figure 6 and conversion by the equilibrium constant. Table III shows our results for the temperature range 300-2300 K in comparison with various experimental results. There is still a considerable uncertainty between the various experimental results. Nevertheless, our values are larger than all experiments. Since, of course, the  $\alpha$  value for the CH<sub>3</sub>O + O exit of the CH<sub>3</sub>O<sub>2</sub> potential surface is unknown, we changed it from the assumed standard value  $\alpha = 1 \text{ Å}^{-1}$  to the value  $\alpha = 1.1 \text{ Å}^{-1}$  of the CH<sub>3</sub>  $+ O_2$  exit. This makes the discrepancy slightly larger. However, from the magnitude of the  $\alpha$  dependence we conclude that an  $\alpha$ value near 0.9 Å<sup>-1</sup> would bring us in agreement with the most recent results of ref 39. Thus, an  $\alpha$  value in the standard range<sup>29</sup>

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 $1 \pm 0.2 \text{ Å}^{-1}$  would favor the data of ref 39. This does not exclude lower rate constants, if there would be peculiarly "rigid anomalies" in the  $CH_3O + O$  exit of the  $CH_3O_2$  surface. Nevertheless, Table III illustrates the large importance of a unimolecular rate analysis for bimolecular reactions involving bound intermediate complexes.

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### Appendix

The vibrational frequencies employed in the calculation are as follows: CH<sub>3</sub>O<sub>2</sub>: 2900, 1350, 960, 2990, 2950, 1400 (2), 900 (2), 450, 1100, and 200 cm<sup>-1.39</sup> CH<sub>3</sub>O: 2930, 2869, 1501, 1325,<sup>42</sup> 1103, 1015,<sup>42</sup> 2947, 1444, and 1155 cm<sup>-1</sup> (calculated in ref 43). CH<sub>3</sub>: 3162 (2), 1396 (2), 3044, and 607 cm<sup>-1.44</sup> O<sub>2</sub>: 1580.2 cm<sup>-1</sup>.45

The following rotational constants were used in the calculation: CH<sub>3</sub>O<sub>2</sub>: A = 1.738, B = 0.404, and C = 0.350 cm<sup>-1.46</sup> CH<sub>3</sub>O: A = 5.328 and B = C = 0.931776 cm<sup>-1.47</sup> CH<sub>3</sub>: A = B = 9.576and  $C = 4.789 \text{ cm}^{-1.44}$  O<sub>2</sub>:  $B_e = 1.4456 \text{ cm}^{-1.45}$ 

The enthalpies for the reaction  $CH_3O_2 \rightarrow CH_3 + O_2$  at 0 K of  $\Delta H0^\circ = 128.4$  kJ mol<sup>-133</sup> and for the reaction  $CH_3O_2 \rightarrow CH_3O$ + O of  $\Delta H_0^{\circ}$  = 249.8 kJ mol<sup>-1 48</sup> were used.

The Lennard-Jones parameters  $\sigma = 4.0$ ,<sup>46</sup> 3.5, and 3.7 Å<sup>49</sup> and  $\epsilon/k = 340,^{46}$  113.5, and 82 K<sup>49</sup> were employed for CH<sub>3</sub>O<sub>2</sub>, Ar, and N<sub>2</sub>, respectively.

Registry No. CH<sub>3</sub>., 2229-07-4; O<sub>2</sub>, 7782-44-7; CH<sub>3</sub>O<sub>2</sub>., 2143-58-0; Ar, 7440-37-1; N<sub>2</sub>, 7727-37-9; azomethane, 503-28-6.

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# Kinetic Analysis of Electroless Deposition of Copper

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Kinetic data on electroless copper deposition from a formaldehyde/EDTA solution are analyzed and discussed in terms of a formal kinetic rate law. The derived rate equation shows first-order dependence on the methylene glycol anion and zeroth order on cupric ion. Kinetic preexponential factors evaluated from temperature dependencies of reaction rates indicate that the rate-determining step involves an adsorbed species. A primary kinetic isotope effect  $k_{\rm H}/k_{\rm D} = 5$  upon substitution of deuterium for protium in formaldehyde indicates that cleavage of the carbon-hydrogen bond of the adsorbed methylene glycol anion is rate determining.

### Introduction

Over the past decade, a number of papers have appeared on the kinetics of electroless copper deposition.<sup>1-8</sup> Both mixed potential analysis<sup>9-11</sup> and classical chemical kinetics<sup>11,12</sup> have been used in attempts to determine the mechanism. To date, the reported overall rate laws have been empirical and have shown nonintegral reaction orders for most reactants.<sup>10-12</sup> Furthermore, as pointed out by Donahue, there is considerable disagreement among various authors as to the reaction order for each species. Part of the reason for this lack of agreement arises from the very

nature of the reaction. At least three processes must occur for the reaction to proceed, the metal ion must diffuse to the surface,

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