

the two dissociation channels in  $\text{CH}_3\text{O}_2$ .

The fact of a much larger  $k(E,J)$  for  $\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3 + \text{O}_2$  compared to  $\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$  implies that the reaction  $\text{CH}_3\text{O} + \text{O} \rightarrow \text{CH}_3\text{O}_2^* \rightarrow \text{CH}_3 + \text{O}_2$  proceeds without any appreciable redissociation of  $\text{CH}_3\text{O}_2^*$ . Therefore, by analogy with the  $\text{HO} + \text{O} \rightarrow \text{HO}_2^* \rightarrow \text{H} + \text{O}_2$  reaction, the rate constant of the reaction  $\text{CH}_3\text{O} + \text{O} \rightarrow \text{CH}_3 + \text{O}_2$  should be identical with the high-pressure recombination rate coefficient for  $\text{CH}_3\text{O} + \text{O} \rightarrow \text{CH}_3\text{O}_2$ . 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  $\text{CH}_3\text{O} + \text{O}$  exit of the  $\text{CH}_3\text{O}_2$  potential surface is unknown, we changed it from the assumed standard value  $\alpha = 1 \text{ \AA}^{-1}$  to the value  $\alpha = 1.1 \text{ \AA}^{-1}$  of the  $\text{CH}_3 + \text{O}_2$  exit. This makes the discrepancy slightly larger. However, from the magnitude of the  $\alpha$  dependence we conclude that an  $\alpha$  value near  $0.9 \text{ \AA}^{-1}$  would bring us in agreement with the most recent results of ref 39. Thus, an  $\alpha$  value in the standard range<sup>29</sup>

(39) H. D. Y. Hsu, W. M. Shaub, T. Craemer, D. Gutman, and M. C. Lin, *Ber. Bunsenges. Phys. Chem.*, **87**, 909 (1983).

(40) T. A. Brabbs and R. S. Brokaw, *Symp. (Int.) Combust.*, [Proc.], **15**, 893 (1975).

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$1 \pm 0.2 \text{ \AA}^{-1}$  would favor the data of ref 39. This does not exclude lower rate constants, if there would be peculiarly "rigid anomalies" in the  $\text{CH}_3\text{O} + \text{O}$  exit of the  $\text{CH}_3\text{O}_2$  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:  $\text{CH}_3\text{O}_2$ : 2900, 1350, 960, 2990, 2950, 1400 (2), 900 (2), 450, 1100, and 200  $\text{cm}^{-1}$ .<sup>39</sup>  $\text{CH}_3\text{O}$ : 2930, 2869, 1501, 1325,<sup>42</sup> 1103, 1015,<sup>42</sup> 2947, 1444, and 1155  $\text{cm}^{-1}$  (calculated in ref 43).  $\text{CH}_3$ : 3162 (2), 1396 (2), 3044, and 607  $\text{cm}^{-1}$ .<sup>44</sup>  $\text{O}_2$ : 1580.2  $\text{cm}^{-1}$ .<sup>45</sup>

The following rotational constants were used in the calculation:  $\text{CH}_3\text{O}_2$ :  $A = 1.738$ ,  $B = 0.404$ , and  $C = 0.350 \text{ cm}^{-1}$ .<sup>46</sup>  $\text{CH}_3\text{O}$ :  $A = 5.328$  and  $B = C = 0.931776 \text{ cm}^{-1}$ .<sup>47</sup>  $\text{CH}_3$ :  $A = B = 9.576$  and  $C = 4.789 \text{ cm}^{-1}$ .<sup>44</sup>  $\text{O}_2$ :  $B_e = 1.4456 \text{ cm}^{-1}$ .<sup>45</sup>

The enthalpies for the reaction  $\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3 + \text{O}_2$  at 0 K of  $\Delta H_0^\circ = 128.4 \text{ kJ mol}^{-1}$ <sup>33</sup> and for the reaction  $\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$  of  $\Delta H_0^\circ = 249.8 \text{ kJ mol}^{-1}$ <sup>48</sup> were used.

The Lennard-Jones parameters  $\sigma = 4.0$ ,<sup>46</sup> 3.5, and  $3.7 \text{ \AA}$ <sup>49</sup> and  $\epsilon/k = 340$ ,<sup>46</sup> 113.5, and  $82 \text{ K}$ <sup>49</sup> were employed for  $\text{CH}_3\text{O}_2$ , Ar, and  $\text{N}_2$ , respectively.

**Registry No.**  $\text{CH}_3$ , 2229-07-4;  $\text{O}_2$ , 7782-44-7;  $\text{CH}_3\text{O}_2$ , 2143-58-0; Ar, 7440-37-1;  $\text{N}_2$ , 7727-37-9; azomethane, 503-28-6.

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## Kinetic Analysis of Electroless Deposition of Copper

R. Schumacher, J. J. Pesek,<sup>†</sup> and O. R. Melroy\*

IBM Research Laboratory, San Jose, California 95193 (Received: February 4, 1985)

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  $k_{\text{H}}/k_{\text{D}} = 5$  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,

(1) A. Molenaar, J. Van Den Meerakker, and J. Boven, *Plating*, **61**, 649 (1974).

(2) F. Donahue, *J. Electrochem. Soc.*, **121**, 887 (1974).

(3) J. Dumesic, J. Koutsky, and T. Chapman, *J. Electrochem. Soc.*, **121**, 1405 (1974).

(4) D. Lax and P. Maughan, *J. Appl. Electrochem.*, **9**, 337 (1978).

(5) S. El-Raghy and A. Abo-Salama, *J. Electrochem. Soc.*, **126**, 171 (1979).

(6) F. Donahue, *J. Electrochem. Soc.*, **127**, 51 (1980).

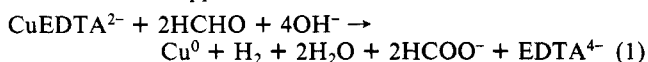
(7) J. Van Den Meerakker, *J. Appl. Electrochem.*, **11**, 387 (1981).

(8) F. Donahue, D. Sajkowski, A. Bosio, and L. Schafer, *J. Electrochem. Soc.*, **129**, 717 (1982).

<sup>†</sup> San Jose State University, Department of Chemistry, One Washington Square, San Jose, CA 95192.

the reducing agent must diffuse to the surface, and a reaction must occur at (or near) the surface resulting in the metal deposition. Under different conditions, any one of these can be rate determining. Another difficulty is the instability of the electroless solutions which limits the range of concentrations over which the kinetics can be studied. As a result, relatively few fundamental studies have been made, and from these, the mechanistic conclusions often conflict.

Electroless copper deposition occurs from alkaline solutions and therefore cupric ions require a chelating agent. In this study, EDTA was chosen as the ligand. As shown by Lukes,<sup>13</sup> the overall reaction at the copper surface is



In the present paper, kinetic data are presented for electroless copper deposition from formaldehyde/EDTA solutions under conditions where the surface reaction is rate limiting and are analyzed to derive a formal kinetic rate law.

### Experimental Section

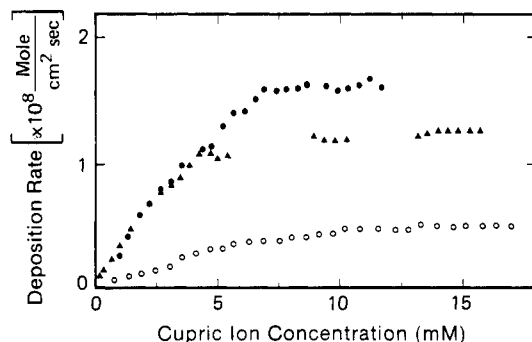
Solutions were prepared from copper sulfate pentahydrate, ethylenediaminetetraacetic acid (EDTA) (both Aldrich gold label), sodium hydroxide, formaldehyde (37 wt % MCB reagent grade), and sodium formate (J. T. Baker reagent grade). Isotopic experiments were carried out with [<sup>13</sup>C]paraformaldehyde (MSDisotopes 92.4 at. % <sup>13</sup>C) and deuterated paraformaldehyde-d<sub>2</sub> (Stohler Isotope Chemicals, 98% deuterium). All reagents were used as received.

Deposition rates were measured in-situ with a quartz crystal microbalance.<sup>14</sup> To avoid induction times, copper was electrolytically deposited on the surface of the microbalance prior to the rate measurements. Measurements made after 30 s of deposition were reproducible within 5%. Experiments were carried out in a 2-L water-jacketed reaction flask in which the temperature was maintained to within 0.1 °C. Kinetic measurements were made while operating under steady-state conditions. To facilitate this, a closed loop control system was constructed in which the concentrations of hydroxide, cupric ions, and the formal concentration of formaldehyde were continuously adjusted. Copper was measured colorimetrically at 730 nm with a Sybron PC 700 colorimeter, pH with an Orion 611 pH meter, and total formaldehyde with a Fiatron SHS 200 flow injection system using a modified Nash reagent. Voltage levels were loaded into an IBM personal computer through a Tecmar Lab Master. The quantity of each reagent required to keep the concentration of the solution constant was computed and sent to digital pipets (SMI Unipump 200) which made the required additions. This was sufficient to maintain concentrations to within 2% over the duration of the experiments.

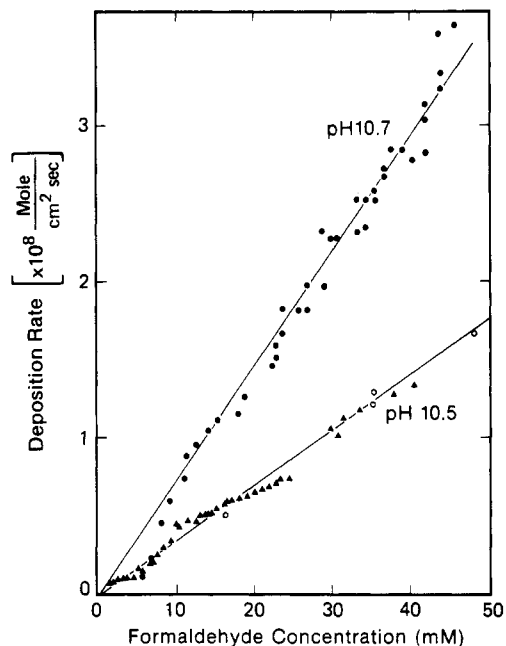
To measure the acid dissociation constant of methylene glycol, we made <sup>13</sup>C NMR measurements on an IBM NR80 multinuclear spectrometer. The sample was placed in a 5-mm insert that was suspended in a 10-mm sample tube containing the chemical shift standard DSS in D<sub>2</sub>O. All chemical shifts are reported relative to the external DSS standard.

### Results

The dependence of the rate of copper deposition (*R*) was studied as a function of the cupric ion, formaldehyde and hydroxide ion concentrations. Although it has previously been reported that the concentration of EDTA affects the rate, the observed reaction order for the ligand was very small (<0.02).<sup>12</sup> In this study, the concentration of EDTA was the same in all experiments. Sodium formate was added to prevent changes in the viscosity and ionic strength of the solution with time and to keep the concentrations of the products constant. Nitrogen was continuously bubbled



**Figure 1.** Deposition rate of copper vs. cupric ion concentration at 70 °C. Solution: EDTA, 0.1 M; sodium formate, 0.25 M, pH 10.5. Formaldehyde: (○) 16 mM, (▲) 35 mM, (●) 48 mM.



**Figure 2.** Deposition rate of copper vs. formaldehyde concentration at 70 °C. Solution: EDTA, 0.1 M; sodium formate, 0.25 M; copper sulfate, 40 mM. Open circles are taken from the plateaus in Figure 1.

through the reaction flask and a magnetic stirring bar provided agitation.

Figure 1 shows the dependence of *R* on the cupric ion concentration at three formaldehyde concentrations. At low copper concentrations (<5 mM), an increase in *R* is observed with increasing cupric ion. However, at higher copper concentrations (>10 mM), the rate is independent of the cupric ion concentration. At low copper concentrations, the rate was strongly dependent on agitation. Increased stirring resulted in an increase of *R*. However, at high copper concentrations the rates were independent on agitation except in the limit of a quiescent solution. Diffusion of copper to the reaction zone limits the reaction rate only at low copper concentrations. At higher copper concentrations, the reaction is kinetically controlled, not mass transport limited, as indicated by the lack of dependence of the rate of agitation. Under kinetically controlled conditions, the reaction is zeroth order in cupric ion concentration.

In order to understand the role of formaldehyde and hydroxide, one must study the kinetics in a region where mass transport of copper does not affect the reaction rate. From Figure 1, one can predict the concentration of copper necessary to meet this condition. However, since higher copper concentrations adversely affect the stability of the solution, it is desirable to use the minimum amount of copper required to ensure that there is no copper mass transport term in the rate. 40 mM cupric solutions were chosen for the formaldehyde studies while 15 mM cupric solutions were used in the hydroxide studies. Care must also be taken in selecting the pH of the solutions since at lower pH's the deposition

(9) F. Donahue, *J. Electrochem. Soc.*, **119**, 72 (1972).

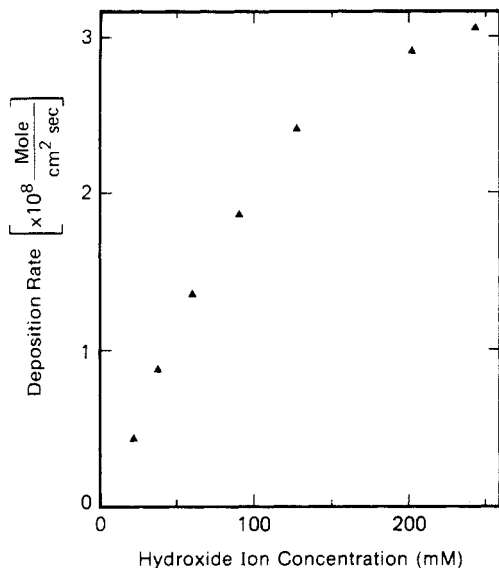
(10) F. Donahue and F. Shippey, *Plating*, **60**, 135 (1973).

(11) F. Donahue, K. Wong, and R. Bhalla, *J. Electrochem. Soc.*, **127**, 2340 (1980).

(12) A. Molenaar, M. Holdrinet, and L. Van Beek, *Plating*, **61**, 238 (1974).

(13) R. Lukes, *Plating*, **51**, 1066 (1964).

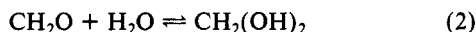
(14) K. K. Kanazawa and J. Gordon, *Anal. Chem.*, in press.



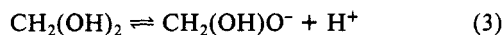
**Figure 3.** Deposition rate of copper vs. hydroxide ion concentration at 70 °C. Solution: EDTA, 0.1 M; sodium formate, 0.25 M; copper sulfate, 15 mM.

rate is slow and thus more difficult to measure while at higher pH values, the solutions are unstable. As shown in Figure 2, at both pH 10.5 and 10.7, the rate is linear in formaldehyde for concentrations between 2 and 40 mM. Under these conditions, the reaction is clearly first order in formaldehyde. In contrast, the rate exhibits a nonlinear dependence on hydroxide as illustrated in Figure 3. From the shape of the curve, it is evident that reaction order for hydroxide is less than one, which suggests a somewhat more complicated role of hydroxide in the reaction mechanism.

In aqueous solutions, formaldehyde can exist in several different forms. Under alkaline conditions, it is almost completely hydrated as methylene glycol (MG).<sup>15</sup>

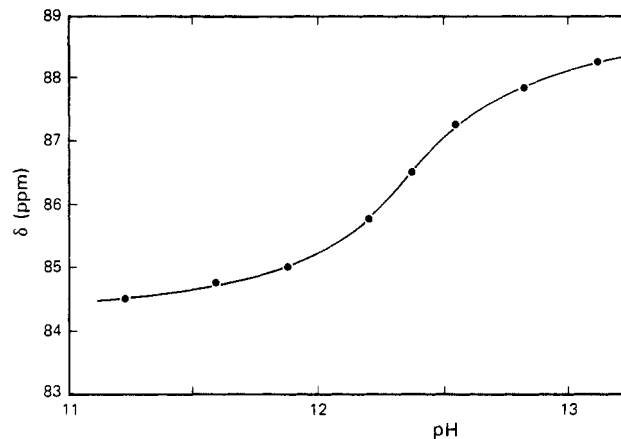


The hydrated form is a weak acid and dissociates.

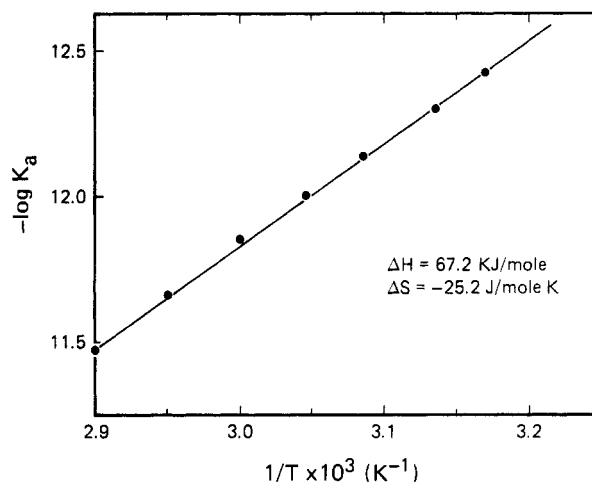


Molenaar et al.<sup>12</sup> have suggested that, at low formaldehyde concentrations, diffusion of the methylene glycol anion (MG<sup>-</sup>) to the reaction zone is the rate-determining step (RDS). Unfortunately, few data exist on the dissociation constant of methylene glycol as a function of temperature. Bell and Onwood<sup>16</sup> and Los et al.<sup>17</sup> determined the log dissociation constant at 25 °C to be 13.27. There have been attempts to determine the equilibrium constant at different temperatures but the measurements are not in complete agreement with each other.<sup>15</sup> Due to the possible importance of the methylene glycol anion, experiments were performed to determine accurately the acid dissociation constant.

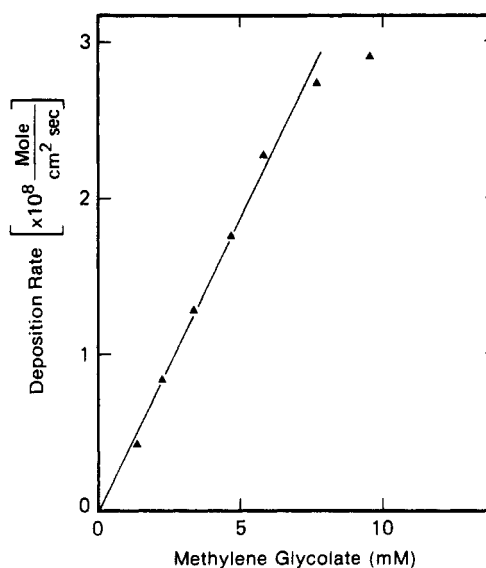
<sup>13</sup>C NMR spectra were measured on 0.07 M <sup>13</sup>C-enriched formaldehyde solutions in 0.5 M sodium sulfate supporting electrolyte over a temperature range of 40 to 70 °C. The low concentration of formaldehyde was used to avoid oligomer formation.<sup>18</sup> Due to the rapid proton exchange between methylene glycol and its anion, the spectrum consists of a single peak whose chemical shift is the weighted average of the shift of both species. A typical plot of the chemical shift vs. pH is shown in Figure 4. At a given temperature, the pK<sub>a</sub> is taken to be the pH of the inflection point in the chemical shift vs. pH graph. The plot of pK<sub>a</sub> vs. 1/T is shown in Figure 5. As expected, the plot is linear and the derived constants for the enthalpy and entropy of reaction are 67.2 kJ/mol and -25.2 J/(mol K), respectively. These values



**Figure 4.** <sup>13</sup>C chemical shift of formaldehyde vs. pH at 40 °C.



**Figure 5.** Log of methylene glycol acid dissociation constant vs. 1/T.



**Figure 6.** Deposition rate of copper vs. methylene glycolate concentration at 70 °C. Data taken from Figure 3.

are well within range normally found for acid dissociations. The extrapolated log dissociation constant at 25 °C is 13.10 which, when considering the difference in ionic strength, is in good agreement with previous measurements.

## Discussion

**Formal Kinetic Analysis.** From the dissociation constants in Figure 5, the concentration of MG<sup>-</sup> as a function of pH can be calculated. In Figure 6, the rate data from Figure 3 is plotted against the MG<sup>-</sup> concentration. The deviation from linearity at

(15) J. Walker, "Formaldehyde", 3rd ed, Reinhold, New York, 1952, p 62.

(16) R. Bell and D. Onwood, *Trans Faraday Soc.*, **58**, 1557 (1962).

(17) J. Los, A. Brinkman, and B. Wetsema, *J. Electroanal. Chem.*, **56**, 187 (1974).

(18) D. Le Botlan, B. Mechin, and G. Martin, *Anal. Chem.*, **55**, 587 (1983).

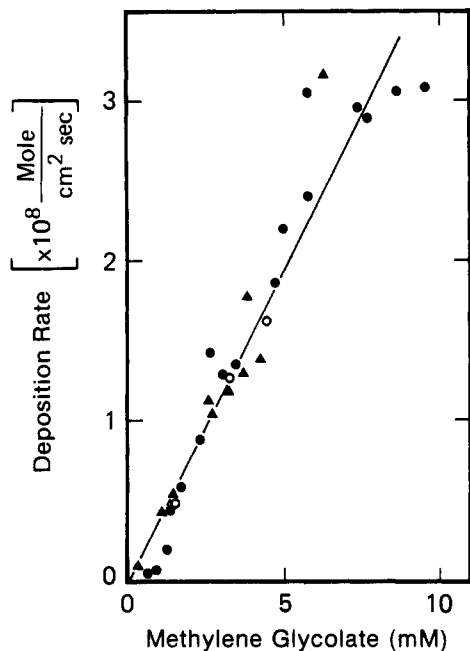


Figure 7. Deposition rate of copper vs. methylene glycolate concentration at 70 °C: (●) obtained at constant formaldehyde concentration with variable pH; (▲) obtained at constant pH with variable formaldehyde concentration; (○) taken from Figure 1.

high rates can be attributed to contributions from mass transfer of copper. Higher copper concentrations could not be used due to the instability of the solution. Rate data from other experiments using different concentrations of formaldehyde and hydroxide are combined and plotted against the  $MG^-$  concentration in Figure 7. All of the data conforms to a very simple Arrhenius type of rate equation which is first order in  $MG^-$  and zeroth order in all other species. The rate equation can be expressed as

$$R = Ae^{-\Delta E^*/RT} C_{MG^-} \quad (4)$$

where  $A$  is the Arrhenius preexponential factor,  $C_{MG^-}$  is the concentration of  $MG^-$  near the surface (surface concentration), and  $\Delta E^*$  is the Arrhenius activation energy. The surface concentration of methylene glycol anion can be assumed to be equal to the bulk concentration under conditions where mass transport is not limiting. Substituting for the formal concentration of formaldehyde  $C_{CH_2O}$ , eq 4 can be rewritten in terms of the formaldehyde and hydroxide concentrations  $C_{OH^-}$  as

$$R = Ae^{-\Delta E^*/RT} \frac{K_a C_{OH^-} C_{CH_2O}}{K_w + K_a C_{OH^-}} \quad (5)$$

**Temperature-Dependent Measurements.** A plot of  $\ln k$  vs.  $1/T$ , where  $k$  is the observed rate constant ( $= Ae^{-\Delta E^*/RT}$ ) is shown in Figure 8 for formaldehyde and formaldehyde- $d_2$  as the reducing agent. Evaluation of the slope gives an activation energy of 60.9 kJ/mol. Molenaar et al.<sup>12</sup> reported an activation energy of 46 kJ/mol but their analysis was based on a rate equation of  $R = k_C^\alpha C_{CH_2O}^\beta C_{Cu^{2+}}^\gamma C_{OH^-}^\delta$ . If the data presented here are analyzed under the same assumption, an activation energy of 40 kJ/mol is obtained. From the Arrhenius plot, it can be seen that upon substitution of deuterium for protium in formaldehyde, the rate decreases by a factor of five. This clearly indicates that hydrogen is a primary reactant in the rate-determining step. The only bonds which are broken or formed involving the hydrogen initially associated with formaldehyde are the cleavage of the carbon-hydrogen bond, and the formation of the hydrogen-hydrogen bond producing  $H_2$ . It is unlikely that formation of the hydrogen-hydrogen bond or the surface mobility of adsorbed hydrogen limits the rate of reaction.<sup>19</sup> It seems reasonable to propose the cleavage of the carbon-hydrogen bond of  $MG^-$  as the rate-determining step

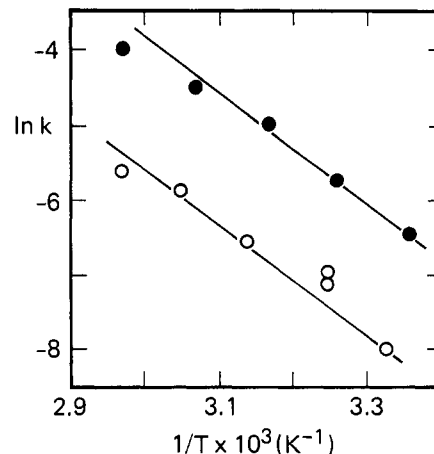


Figure 8. Log of observed rate constant vs.  $1/T$  for  $CH_2O$  (●) and  $CD_2O$  (○).

for the kinetically controlled process.

From Figure 8, one can see that, upon isotopic substitution, the rate changes but the activation energy does not. The change in rate is entirely accounted for by a change in the preexponential factor  $A$ . As will be shown below, this fact, coupled with the magnitude of  $A$ , strongly suggests that  $MG^-$  is adsorbed on the surface prior to dissociation.

Using the activated complex theory, a collision factor  $Z$ , a transmission factor  $\kappa$ , and an entropy and enthalpy of activation  $\Delta S^*$  and  $\Delta H^*$ , we can write eq 4 as

$$R = \kappa Z e^{\Delta S^*/R} e^{-\Delta H^*/RT} C_{MG^-} \quad (6)$$

The transmission coefficient is usually taken to be unity and the entropy of activation assumed to be zero. Even in reactions where the activated complex involves some rearrangement of atoms, the factor ( $e^{\Delta S^*/R}$ ) is rarely observed to be larger than  $10^2$  or less than  $10^{-2}$ . For electrode reactions which do not involve adsorbed intermediates, the expected collision frequency  $Z_{el}$  can be calculated from Marcus theory<sup>20</sup> as

$$Z_{el} = \left( \frac{kT}{2\pi m} \right)^{1/2} \quad (7)$$

where  $m$  is the molecular weight of the diffusing reactant. For  $MG^-$  at temperature of 330 K, the predicted collision frequency is  $9.4 \times 10^5$  cm/s. This is significantly smaller than the observed collision frequency of  $7.5 \times 10^7$  cm/s for formaldehyde and  $1.5 \times 10^7$  cm/s for deuterated formaldehyde. The lack of agreement between Marcus theory and the experiment suggests that the rate-limiting step involves an adsorbed species rather than a freely diffusing species.

Anson and Brown<sup>21</sup> studied electron transfer kinetics for reactants adsorbed on graphite electrodes and showed that the kinetics could be described as

$$R_s = \kappa Z_s e^{-\Delta G_s^*/RT} \Gamma \quad (8)$$

where  $\Delta G_s^*$  is the free energy of activation of the adsorbed reactant,  $\Gamma$  is the surface coverage, and  $Z_s$  is the collision frequency for the adsorbed species with the electrode. The upper limit for this collision frequency was predicted to be

$$Z_s = kT/h \quad (9)$$

which can be rationalized in terms of intramolecular vibrational frequencies. At 330 K, the value for  $Z_s$  is  $6.6 \times 10^{12}$  L/s. To see if a rate-determining step involving adsorbed  $MG^-$  is reasonable, a coverage can be estimated by equating eq 6 and 8 to obtain

$$\Gamma = \frac{Z_{el}}{Z_s} e^{(\Delta G_s^* - \Delta E^*)/RT} C_{MG^-} \quad (10)$$

(20) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1964).

(21) A. P. Brown and F. C. Anson, *J. Electroanal. Chem.*, **92**, 133 (1978).

(22) R. Van Effen and D. Evans, *J. Electroanal. Chem.*, **107**, 405 (1980).

(19) M. Balooch, M. Cardillo, D. Miller, and R. Stickney, *Surf. Sci.*, **46**, 358 (1974).

Using the observed value of  $7.5 \times 10^7$  cm/s for  $Z_{el}$ , a bulk concentration of  $MG^-$  equal to  $6 \times 10^{18}$  molecules/cm<sup>3</sup> (an average value from Figure 7) and the upper limit of  $6.6 \times 10^{12}$  L/s for  $Z_s$ , one obtains a coverage of  $6.8 \times 10^{13}$  molecules/cm<sup>2</sup>. The exponential term is taken as unity since, assuming the rate-determining step involves an adsorbed species, the observed free energy of activation is the free energy of activation for the adsorbed reactant. If we assume that one molecule of  $MG^-$  occupies  $10 \text{ \AA}^2$ , this corresponds to a steady-state fractional coverage of 0.07.

Although this estimated coverage cannot be considered quantitative, it is consistent with the first-order dependence seen for bulk  $MG^-$ . At higher coverages, saturation of the surface should result in independence of rate on  $MG^-$ . These conditions, however, are not achieved because a high copper concentration would be needed to maintain kinetic control at the high reaction rates achieved at the high  $MG^-$  concentrations required to saturate the copper surface. Clearly, the first-order dependence on  $MG^-$  is inconsistent with a saturated coverage of  $MG^-$ . As previously mentioned, at high concentrations of hydroxide, formaldehyde, and copper, the solution is unstable and formation of copper metal occurs spontaneously in solution.

The change in  $Z$  upon substitution of deuterium for protium in formaldehyde is also consistent with cleavage of the carbon-hydrogen bond of an adsorbed  $MG^-$  as the rate-determining step. The experimental collision frequencies for formaldehyde and formaldehyde- $d_2$  quoted in the previous section assumed  $\kappa = 1$  and  $\Delta S^\ddagger = 0$  and therefore could be in error by as much as a factor of  $10^2$ . The relative magnitudes of the two, however,  $Z_{CH_2O}/Z_{CD_2O} = 5$  should be correct since it is unlikely that  $\kappa$ ,  $\Gamma$ , or  $\Delta S^\ddagger$  change significantly upon isotopic substitution. For example, a difference of  $13 \text{ J/(mol K)}$  in  $\Delta S^\ddagger$  would be required to account for the factor

of five in the rate. From eq 7,  $Z_{el}$  depends only on the molecular weight of the diffusing species. Substitution of deuterium for protium in formaldehyde only reduces  $Z_{el}$  by 2%. For an adsorbed species, however,  $Z_s$  is related to the vibrational frequencies of the molecule and should be strongly affected by isotopic substitution.

Recently, Evans et al.<sup>21</sup> reported a primary isotope effect  $k_H/k_D = 3-4$  for the oxidation of various aldehydes on gold in alkaline solutions. The proposed mechanism was based on a dissociative adsorption step with cleavage of the  $\alpha$ -carbon-hydrogen bond. Although the electroless process does not appear to be a dissociative adsorption step but rather dissociation following adsorption, the results of Evans seem to be in good agreement with the observations in this study.

### Conclusion

Under conditions where the electroless deposition of copper is kinetically controlled, the reaction is first order in methylene glycolate and zeroth order in all other reactants. Temperature-dependent measurements and isotopic substitution yield an activation energy of  $60.9 \text{ kJ/mol}$  and a primary kinetic isotopic effect  $k_H/k_D = 5$ . Indications are that the rate-determining step involves cleavage of a carbon-hydrogen bond of adsorbed methylene glycolate. The acid dissociation constant of methylene glycol has been measured between  $40$  and  $70 \text{ }^\circ\text{C}$ .  $\Delta H$  was found to be  $67.2 \text{ kJ/mol}$  with a  $\Delta S$  of  $-25.2 \text{ J/(mol K)}$ .

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**Registry No.** EDTA, 60-00-4; HCHO, 50-00-0; Cu, 7440-50-8; deuterium, 7782-39-0.

## Free Radical and Free Atom Reactions in the Sonolysis of Aqueous Iodide and Formate Solutions

Edwin J. Hart and Arnim Henglein\*

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany (Received: March 13, 1985)

Solutions of potassium iodide and sodium formate were irradiated with 300-kHz ultrasound and the products analyzed. The irradiations were carried out under atmospheres of argon, oxygen, and argon-oxygen mixtures of varying composition. In addition, experiments with pure water and water containing ozone were undertaken. The products of irradiation of iodide solutions are iodine and hydrogen peroxide; hydrogen is also formed in the absence of oxygen. With an atmosphere of 70% argon and 30% oxygen, the yields are drastically higher than for irradiation under pure argon or oxygen. The products of the irradiation of formate solutions are hydrogen, carbon dioxide, hydrogen peroxide, and oxalate in the absence of  $O_2$  and hydrogen peroxide and carbon dioxide in the presence of  $O_2$ . A strong enhancement of the yields is also observed for formate solutions containing both argon and oxygen. Ozone could not be identified as a stable product of the irradiation of oxygenated water. On the contrary, water containing ozone was found to rapidly lose  $O_3$  upon ultrasonic irradiation. The dependence of the yields of the various products on the concentration of the dissolved substances was studied in order to derive a mechanism of the chemical action of ultrasound. The results are explained in terms of the formation of H and OH radicals in the gas bubbles. In the absence of oxygen, the H atoms form  $H_2$  and the OH radicals form hydrogen peroxide or react with nonvolatile substrates in the interfacial region. In the presence of oxygen,  $HO_2$  radicals, OH radicals, and O atoms are formed. The  $HO_2$  radicals do not attack iodide or formate but produce hydrogen peroxide. Oxygen atoms are scavenged by iodide and formate ions. An appreciable concentration of the superoxide radical anion,  $O_2^-$ , was detected after the irradiation of an oxygenated,  $10^{-2} \text{ M}$  formate solution of pH 14. The  $O_2^-$  anion decayed after irradiation with a half-life of 3 min.

### Introduction

Free radicals such as hydrogen atoms and hydroxyl radicals are known to be generated upon the action of ultrasonic waves on aqueous solutions.<sup>1-4</sup> The chemical effects are brought about in the presence of a monoatomic or diatomic gas. They are due

to the high temperatures of several 1000 K and pressures of some 100 bar which exist in the compression phase of oscillating or

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\* To whom correspondence should be addressed.