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## Kinetics of the Thallic Ion Oxidation of Olefins.

### I. Salt Effects on the Oxidation of Ethylene

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The oxidation of ethylene,  $Tl^{+3} + CH_2=CH_2 (H_2O) \rightarrow CH_3CHO + (CH_2OH)_2$ , is first order in ethylene, first order in thallic ion, and strongly accelerated by increasing salt concentration. This acceleration is of the type previously observed for the mercuration of benzene; i.e., the rate constant is an inverse function of the activity of water. This reaction is thus another example of the activation of metal ions by dehydration. The order of magnitude of the effect in various media, perchlorate > sulfate > nitrate, can be explained by deactivation of the metal ion by ion-pair formation. A mechanism for the reaction is proposed in terms of  $\pi$ - and  $\sigma$ -bonded intermediates, and the possible identity of the step of the mechanism most affected by the rate acceleration is discussed.

Recently, aqueous thallic ion was reported to oxidize olefins to glycols and carbonyl compounds,<sup>1</sup> whereas, in acetic acid and methanol, 1,1- and 1,2-disubstituted as well as allylic oxidation products are found.<sup>2-4</sup> Although the mechanism of the allylic oxidation is uncertain, the evidence suggests that the other products arise from the oxidative decomposition of a  $\sigma$ -bonded oxythallation adduct analogous to the stable product of oxymercuration of olefins.<sup>5</sup>

This paper describes a kinetic study of the oxidation of ethylene in aqueous solution. Of special concern are the large salt effects observed for this reaction. Rate acceleration of the same magnitude has been observed for some reactions of aqueous mercuric ion with unsaturated organic molecules.<sup>6,7</sup>

Perrin and Westheimer<sup>8</sup> have demonstrated that for mercuration of benzene the rate acceleration is not related to acidity but rather is an inverse function of the water activity.

#### Results

The reaction was studied in aqueous sulfuric, nitric, and perchloric acids as well as in mixtures of per-

chloric acid and sodium perchlorate. All rates were measured by ethylene uptake and most runs were made at a constant ethylene pressure of 1 atm.

*Order of Reaction and Products.* Plotting the data at atmospheric pressure as first-order reactions, presuming the decrease in thallic ion concentration is proportional to the ethylene uptake, gave linear plots indicating that the reaction is first order in thallic ion. The final reaction mixtures contained no thallic ion and the number of moles of ethylene taken up in excess of solubility was equal to the number of moles of thallic ion reduced.

The order of ethylene was determined by running several reactions in a constant volume reactor.<sup>9</sup> When the data were plotted as a reaction first order in ethylene and first order in thallic ion, linear plots were obtained, proving the validity of the assumption. The second-order rate constants agreed well with those obtained in atmospheric pressure runs (see Table I).

Table I. Kinetic Data. Perchlorate System

HClO <sub>4</sub> , M	NaClO <sub>4</sub> , M	Solubility of ethylene, mM	$k_2$ , <sup>a</sup> M <sup>-1</sup> sec. <sup>-1</sup>	-Log $a_{H_2O}$
0.35	...	4.72	0.45	0.006
0.50 <sup>b</sup>	...	4.64	0.63	0.009
0.85	...	4.45	0.75	0.015
1.35	...	4.30	0.97	0.026
0.5	1.0	3.40	1.35	0.029
1.5	...	4.25	1.08	0.030
1.85	...	4.14	1.53	0.039
1.15	1.12	2.85	2.50	0.045
0.5	2.0	2.70	2.67	0.048
2.25	...	4.01	2.17	0.052
2.5	...	3.93	3.08	0.061
2.5 <sup>b</sup>	...	3.93	2.97	0.061
0.35	3.0	2.15	4.84	0.067
1.15	2.12	2.20	4.67	0.070
0.5	3.0	2.05	6.17	0.071
2.75	...	3.85	4.50	0.072
3.0	...	3.76	5.59	0.082
0.5	3.5	1.82	8.51	0.087
3.25	...	3.69	7.18	0.094
0.5	4.0	1.60	13.0	0.103
3.5	...	3.61	8.25	0.106
3.75	...	3.53	9.34	0.119
0.5	5.0	1.08	25.5	0.134
4.0	...	3.45	12.1	0.135
4.25	...	3.37	13.2	0.156
0.5	5.5	0.9	40.0	0.159

<sup>a</sup> Most of these values are an average of at least two runs.

<sup>b</sup> Run in constant volume reactor.

(9) P. M. Henry, *ibid.*, **86**, 3246 (1964).

- (1) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).
- (2) C. B. Anderson and S. Winstein, *ibid.*, **28**, 605 (1963).
- (3) H. J. Kabbe, *Ann.*, **656**, 204 (1962).
- (4) J. B. Lee and M. J. Price, *Tetrahedron Letters*, **24**, 1155 (1962).
- (5) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).
- (6) R. M. Schramm, W. Klapproth, and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).
- (7) K. Schwabe and J. Voigt, *Z. physik. Chem. (Leipzig)*, **203**, 383 (1954).
- (8) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2773 (1963).

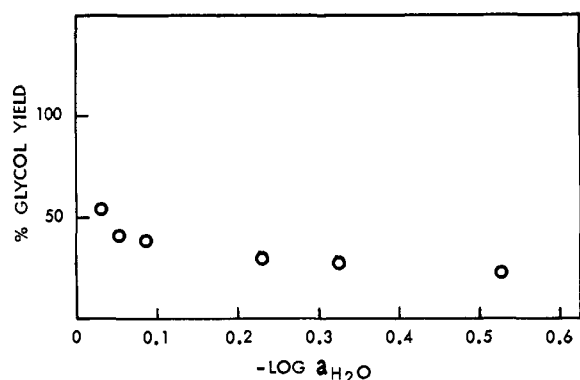


Figure 1. Glycol yield vs. the negative logarithm of the activity of water.

As reported previously,<sup>1</sup> the only products initially formed were acetaldehyde and ethylene glycol. Under the experimental conditions employed, the combined yield of these two products was above 90%, the remainder being accounted for by further oxidation of the initial products. The ratio of glycol to acetaldehyde was a little over 1:1 in the perchlorate system at lower electrolyte concentrations. However, the glycol yield decreased with decreasing water activity as is shown in Figure 1.

In several runs, sodium sulfate was added to the sulfuric acid system to test the effect on rate. The rate was definitely retarded but the nature of the reaction changed.<sup>10</sup>

**Salt Effects.** Using a reactor with high-speed stirring,<sup>9</sup> the shortest half-lives which could be measured accurately were 10–15 sec. This limited the range of water activities which could be covered. For the perchlorate system (Table I) the range of  $\log a_{H_2O}$  was 0 to  $-0.15$ , whereas for the sulfuric acid system (Table II) it was 0 to  $-0.3$ . The water activities of the pure acid systems were taken from the tables of Bunnett.<sup>11</sup> The water activities of the mixed sodium perchlorate-perchloric acid reaction mixtures were calculated, making use of the observation<sup>8</sup> that the isopiestic contours are nearly straight lines in the  $M$

Table II. Kinetic Data. Sulfate System

$H_2SO_4$ , $M$	Solubility of ethylene, $mM$	$k_2$ , <sup>a</sup> $M^{-1} \text{ sec.}^{-1}$	$-\log$ $a_{H_2O}$
0.8	3.95	0.72	0.014
1.25	3.43	0.88	0.025
1.75	3.05	1.15	0.037
2.5	2.45	2.4	0.063
3.5	2.13	5.1	0.110
4.5	1.93	9.6	0.177
4.8	1.85	16.3	0.201
5.5	1.75	20.5	0.268
5.9	1.68	34.7	0.311

<sup>a</sup> Most of these values are an average of at least two runs.

$HClO_4$ - $M$   $NaClO_4$  plane. The water activities used for the sodium perchlorate solutions were calculated from the data of Miller and Sheridan.<sup>12</sup> Where

(10) P. M. Henry, unpublished data.

(11) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).

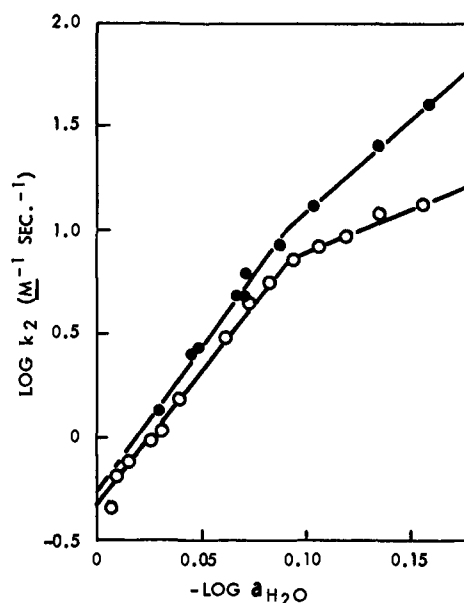


Figure 2. The logarithm of the second-order rate constant vs the negative logarithm of the activity of water for the perchlorate system: O,  $HClO_4$ ; ●,  $HClO_4$ - $NaClO_4$ .

comparison is possible these values are in reasonably good agreement with those of Perrin and Westheimer at  $40^\circ$ .<sup>8</sup>

The data for the  $HClO_4$ - $NaClO_4$  and  $HClO_4$  systems were plotted both as  $\log$  of the second-order rate constant  $k_2$  vs.  $-\log a_{H_2O}$  (Figure 2) and  $\log$  of the pseudo-first-order rate constant  $k_1$  at constant ethylene pressure of 1 atm. vs.  $-\log a_{H_2O}$  (Figure 3) to demonstrate that the two systems fall more nearly on the same curve when  $k_1$  is used. The initial slopes in Figure 2 are about 15 for both with final slopes of 9 for the  $HClO_4$ - $NaClO_4$  systems and 5 for the  $HClO_4$  system. In Figure 3 both plots have initial slopes of about 13 and final slopes of 4.

A plot of  $\log k_2$  vs.  $-\log a_{H_2O}$  for the sulfuric acid system (Table II) is shown in Figure 4. Here the initial slope is 9 and the final slope 4.

Table III. Kinetic Data. Nitrate and Mixed Perchlorate-Nitrate Systems

$HNO_3$ , $M$	$HClO_4$ , $M$	Solubility of ethylene, $mM$	$k_2$ , $M^{-1}$ $\text{sec.}^{-1}$	$-\log$ $a_{H_2O}$
1.5	...	4.48	0.82	0.025
2.5	...	4.34	1.18	0.049
3.5	...	4.21	1.73	...
4.5	...	4.08	2.59	...
0.5	4.0	3.51	5.9	...
2.0	2.5	3.75	6.3	...

The data for the nitric acid system (Table III) were not plotted since good data for the water activity of nitric acid are not available above 2.5  $M$ . Included in the table are rate constants for mixed  $HNO_3$ - $HClO_4$  solutions.

No  $H_0$  or  $H_R$  values were determined in this work, but several of the reaction mixtures were almost identical

(12) M. L. Miller and C. L. Sheridan, *J. Phys. Chem.*, **60**, 184, 186 (1956).

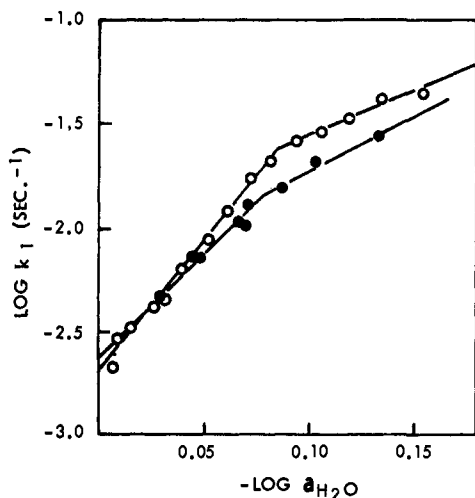


Figure 3. The logarithm of the first-order rate constant vs. the negative logarithm of the activity of water for the perchlorate system: O,  $\text{HClO}_4$ ; ●,  $\text{HClO}_4\text{-NaClO}_4$ .

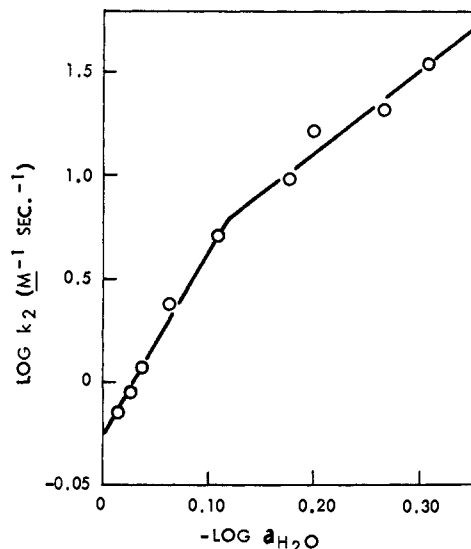


Figure 4. The logarithm of the second-order rate constant vs. the activity of water for the sulfate system.

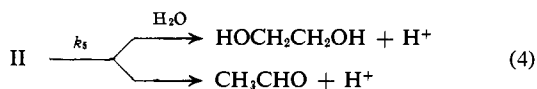
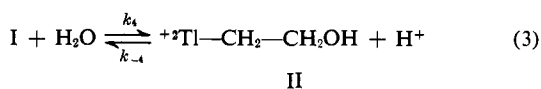
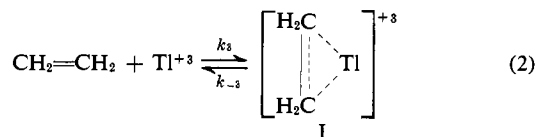
with those of Perrin and Westheimer for which these functions were evaluated; comparing  $H_0$  and  $H_R$  and  $\log a_{\text{H}_2\text{O}}$  with rate constants for these reaction mixtures indicated that there was no correlation of rate with  $H_0$  and  $H_R$ .

Since the rate is first order in thallic ion and ethylene and does not depend on acid concentration as such, the rate expression is

$$-\frac{d[\text{Ti}^{+3}]}{dt} = k_2[\text{Ti}^{+3}][\text{C}_2\text{H}_4] \quad (1)$$

### Discussion

On the basis of present evidence the following reaction sequence appears to be the most reasonable.



The evidence for this mechanism is summarized as follows. (1) Intermediates corresponding to II have been isolated.<sup>2,3,13</sup> (2) Oxymercuration as well as deoxymercuration are postulated to proceed through  $\pi$ -complexes such as I,<sup>5,14,15</sup> and recently kinetic evidence for such an intermediate has been found.<sup>10</sup> (3) Other metal ion oxidations appear to proceed by similar routes.<sup>3,9</sup> (4) Stereochemistry of products suggests an intermediate such as II.<sup>2</sup>

Since the rate expression for this reaction (eq. 1) does not contain a term involving inhibition by proton, the equilibrium represented by eq. 3 is not established. Thus, either  $k_3$  or  $k_4$  would have to be rate determining.

(13) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

(14) P. Brandt and O. Plum, *Acta Chem. Scand.*, **7**, 97 (1953).

(15) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).

On the basis of present evidence it is difficult to decide which. Perhaps  $k_4$  is to be preferred since  $\pi$ -complex formation is usually a rapid reaction.<sup>9,16,17</sup>

The relationship between rate and water activity for the thallic ion oxidation of ethylene is very similar to that found for the mercuration of benzene<sup>8</sup> and there is little doubt that the basis for this effect is the same in both cases. Both reactions involve the attack of metal ions on unsaturated organic molecules and both probably involve  $\pi$ - and  $\sigma$ -bonded intermediates.<sup>18</sup> In the mercuration of benzene,<sup>8</sup> the rate of deprotonation of a  $\sigma$ -complex could be shown by deuterium isotope effects to be rate determining, and most of the rate acceleration with decreasing water activity resulted from the acceleration of the rate of formation of the  $\sigma$ -complex rather than the deprotonation.

Thus in both reactions either formation of  $\pi$ -complex or rearrangement of  $\pi$ -complex to  $\sigma$ -complex could be the step most influenced by the salt effects. The present evidence does not permit a choice between the two.<sup>19</sup>

Formulating the problem in terms of activity coefficients, we can write

$$k/k_0 = \frac{f_{\text{C}_2\text{H}_4}f_{\text{Ti}^{+3}}}{f^*} \quad (5)$$

where  $k_0$  is the rate constant at the thermodynamic reference state.

If an intermediate is reversibly formed,  $m_0$  and  $M_0$  functions<sup>8</sup> analogous to the  $h_0$  and  $H_0$  functions can be written

$$M_0 = -\log m_0 = -\log a_{\text{M}^{+n}}f_{\text{S}}/f_{\text{SM}^{+n}} \quad (6)$$

(16) P. Brandt, *Acta Chem. Scand.*, **13**, 1639 (1959).

(17) Data on the variation of rate with olefin structure<sup>10</sup> are not entirely consistent with the postulate that  $k_4$  is rate determining, so the reaction may be more complicated than the mechanism proposed in eq. 2-4.

(18) A. W. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 11.

(19) Recently it was reported (B. B. Baker, *Inorg. Chem.*, **3**, 200 (1964)) that the  $\pi$ -complex formation between  $\text{Ag}^+$  and ethylene was favored by lowering the water activity.

where S is an organic substrate which reversibly forms either a  $\pi$ - or  $\sigma$ -bonded intermediate depending on which intermediate is reversibly formed in the reaction in question. The complete rate expression is then

$$k = \frac{k'}{K_m} m_0 \frac{f_{BM^{+n}} f_B}{f_S f^*} \quad (7)$$

where B is the organic reactant,  $BM^{+n}$  is the intermediate,  $K_m = a_B a_{M^{+n}} / a_{BM^{+n}}$ , and  $k'$  is the rate constant for reaction of  $BM^{+n}$ . Since suitable indicators are not available,  $M_0$  can only be defined in terms of a particular reaction, as was done for the mercuration of benzene.<sup>8</sup>

The source of the variation of  $m_0$  with increasing electrolyte concentration, and therefore of the rate acceleration, may be regarded from two viewpoints: hydration changes explicitly, or changes in the ratio of activity coefficients in eq. 5, 6, and 7 which are related to hydration changes.

The arguments for the first viewpoint follow those recently advanced for the  $H_0$  function.<sup>20-23</sup> The changes in water of hydration is going from reactants to products is taken into account in writing eq. 5, 6, and 7, so that the expressions contain a term in  $(a_{H_2O})^n$ , where  $n$  is associated with the net hydration change. The slope of a plot of  $-\log k$  vs.  $\log a_{H_2O}$  is thus related to this change in hydration. In this treatment the ratio of activity coefficients of species of equal charge is presumed to be unity.

The second viewpoint focuses on the activity coefficients themselves. The argument here is that small metal ions would be affected much more by increasing salt concentration than are intermediate complexes in which the charge is much more diffuse. Thus the rate acceleration is regarded as being due to the raising of the activity coefficient of the metal ion reactant relative to that for the activated complex or reactive intermediates. The changes in these activity coefficients would indeed be related to energies of hydration (the large increase in activity coefficients of metal perchlorates is explained by hydration changes<sup>24</sup>) and thus to water activity, but the slopes of the plots cannot be identified explicitly with numbers of water molecules released.

Recently these two viewpoints were combined in calculations of Tigue<sup>25</sup> who considered the effect of differences of hydration of reactants and intermediates on the ratio of activity coefficients. Considering only the entropy contribution to the activity coefficients, Tigue was able to explain satisfactorily the changes in  $H_0$  and  $-\log [H^+]$  as the water activity decreased. However, for  $H_R$  the agreement was not as good, indicating that the electrostatic contributions to the change in activity coefficients are important. Certainly for metal ions such as thallic and mercuric, the electrostatic contribution to the activity coefficients would be even more important. Because of the size parameter,<sup>26</sup>

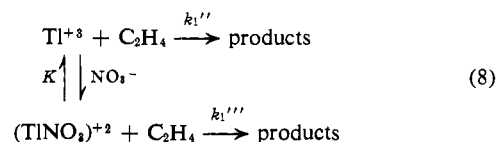
the electrostatic contributions to the activity coefficients will change in a different way with salt concentration for the metal ion and intermediate, and thus the ratio of activity coefficients will change. In addition, there is the complication that the size of the ions changes with water activities due to changes in hydration.<sup>27</sup>

It would be interesting to compare the  $M_0$  for a metal defined in terms of one reaction with the values found for a different reaction. For mercuric ion, for example, the  $Hg_0$  are found for the mercuration of benzene could be compared with that found for acetylene hydration which has also been shown to exhibit strong salt effects.<sup>7,28</sup>

If the  $M_0$ 's as defined for several reactions are very similar, the  $M_0$  function would have general utility in predicting salt effects in metal ion reactions. This similarity might be expected if the step most accelerated by decreasing water activity (*i.e.*, metal + organic substrate to  $\pi$ -complex) is the same in each case. Alternately, if the main cause for the acceleration is an increase in the activity coefficient of the metal ion,  $M_0$  would be expected to be independent of the reaction used to define it.

Differences between the perchlorate, sulfate, and nitrate system can be explained on the basis of retardation of rate by ion-pair formation. The order of magnitude of the acceleration (perchlorate > sulfate > nitrate), the same as that found for the mercuration of benzene, is in the order of decreasing amount of ion-pair formation expected in these systems.<sup>29</sup> Inhibition of rate by addition of sulfate ions to the sulfuric acid system and the decrease in rate observed when perchloric acid is replaced by nitric acid are consistent with this assumption.

Assuming the following path in the nitrate system



and assigning the values  $K = 3$  (a value in the range found for ion-pair formation in this system<sup>30</sup>) and the first-order rate constants  $k_1'' = 1.6 \times 10^{-2} \text{ sec.}^{-1}$  (the extrapolated value for 4.5 M HClO<sub>4</sub> from Figure 3) and  $k_1''' = 2 \times 10^{-3} \text{ sec.}^{-1}$ , the values of  $k_1$  given in Table IV can be calculated. The agreement is good considering that the assumption of constant  $k_1''$ ,  $k_1'''$ , and  $K$  cannot be strictly true.

The decrease of glycol yield with decreasing water activity (Figure 1) is expected, since water is required to form glycol but is not required to form acetaldehyde from the intermediate (II).

The better agreement between the NaClO<sub>4</sub>-HClO<sub>4</sub> and HClO<sub>4</sub> systems when  $k_1$  rather than  $k_2$  is plotted vs.

(27) The change in ultraviolet spectra of thallic ion in perchlorate media with changes in perchlorate concentration has been interpreted (T. E. Rodgers and G. M. Waind, *Trans. Faraday Soc.*, **57**, 1360 (1961)) in terms of hydration changes.

(28) A recent study (W. L. Budde and R. E. Dessy, *J. Am. Chem. Soc.*, **85**, 3964 (1963)) has emphasized the importance of water activity in this reaction.

(29) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, Burlington House, W1, London, 1958.

(30) E. A. Burns and R. A. Whitaker, *J. Am. Chem. Soc.*, **79**, 866 (1957).

(20) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4973 (1961).

(21) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

(22) P. A. H. Wyatt, *ibid.*, **24**, 162 (1957).

(23) C. Perrin, *J. Am. Chem. Soc.*, **86**, 256 (1964).

(24) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, Chapter 8.

(25) P. T. Tigue, *Trans. Faraday Soc.*, **60**, 127 (1964).

(26) E. Glueckauf, *ibid.*, **51**, 1235 (1955).

Table IV. Calculated and Experimental Values of  $k$  in  $\text{HClO}_4\text{-HNO}_3$  Mixtures

$\text{HNO}_3$	$k_1, \text{sec.}^{-1} \times 10^2$	
	Calcd.	Exptl.
0.5	0.76	0.68
2.0	0.40	0.47
4.5	0.30	0.27

water activity (compare Figures 2 and 3) is not surprising since the  $k_1$  values compare the rates at constant ethylene activity. The difference between the two when  $k_1$  is used means that water activity is not the only factor, but that the ratio of activity coefficients also depends on the particular electrolyte. The differences are small, however, when compared to the effect of water activity.

Comparison of these salt effects with those found in the  $\text{Tl(III)-Tl(I)}$  exchange shows that the effects are quite different from those found here for the thallic ion oxidation of ethylene. Perchlorate ion decreases the rate<sup>31</sup> while nitrate<sup>32</sup> and sulfate<sup>33</sup> accelerate the rate of exchange. This result can be explained on the basis of the competitive effect of lowering of water activity and ion-pair formation. In the perchlorate system, a poor complex former, the important factor is the solvation of the activated complex which involves the approach of two positive ions. Decreasing water activity raises the energy of the activated complex relative to that of the separated metal ions. The ability of the nitrate and sulfate to form bridging groups outweighs the effect of lowered water activity.<sup>31</sup>

#### Experimental

**Reagents.** The thallic ion solutions were prepared by dissolving thallic oxide (Fairmount Chemical Co.) in the appropriate acid. The solutions were analyzed either polarographically or by treatment with potassium

(31) S. W. Gilks and G. M. Waind, *Discussions Faraday Soc.*, 29, 102 (1960).

(32) R. J. Prestwood and A. C. Wahl, *J. Am. Chem. Soc.*, 71, 3137 (1949).

(33) C. H. Brubaker and J. P. Mickel, *J. Inorg. Nucl. Chem.*, 4, 55 (1957).

iodide followed by titration with standard thiosulfate. All salts were of reagent grade.

**Analysis of Reaction Mixtures.** Several reaction mixtures were analyzed to determine distribution of products. Carbonyl compounds and thallic and thallic ions were analyzed polarographically while glycol was analyzed either by the periodate method<sup>34</sup> or by vapor phase chromatography using a 1-ft. Carbowax 4000 on Fluoropak 80 column and programming from 100 to 225° at a rate of 18°/min.<sup>35</sup>

When rapid stirring and low concentrations (<0.1  $M$ ) of thallic ion were employed, practically the only carbonyl compound found was acetaldehyde (identified by vapor phase chromatography and mass spectrophotometric analysis). At higher thallic ion concentrations, appreciable amounts of another carbonyl compound could be detected polarographically. This carbonyl was identified as glyoxal by paper chromatography.

At low salt concentrations in the perchloric acid system, the yield of acetaldehyde was between 35–40% while the yield of ethylene glycol was between 45–55%. Figure 1 gives the yield of ethylene glycol as a function of water activity.

**Kinetic Runs.** All kinetic procedures have been described previously.<sup>9</sup> Most rates were determined by measuring the ethylene uptake at a constant ethylene pressure of 1 atm. using gas burets. Creased flasks with agitation by magnetic stirring bars were used as reaction vessel for the slower runs and a high speed stirred reactor for the faster runs. To determine order in ethylene, two runs were made in a constant volume reactor.

**Acknowledgment.** The author gratefully acknowledges helpful discussion with Dr. H. G. Tennent and Professors M. Kilpatrick, S. Winstein, and H. Taube. The author also acknowledges the assistance of Mr. John Jackson with experimental work.

(34) G. O. Curme, "Glycols," Reinhold Publishing Corp., New York, N. Y., 1952, p. 337.

(35) The author is indebted to Dr. G. A. Ward of the Hercules Research Center for developing this procedure.