TABLE I

ACID DISSOCIATION CONSTANTS OF THIOUREA ANALOGS IN 50% BY VOLUME DIOXANE AT 25°

		pK_a			pK_a
1	Thiourea	2.03	7	*o*-Tolylthiourea	2.78
2	Urea	1.40	8	*m*-Tolylthiourea	2.70
3	Allylthiourea	2.48	9	*p*-Tolylthiourea	2.72
4	Ethylthiourea	2.85	10	Ethylenethiourea	2.70
5	Methylthiourea	2.90	11	*sym*-Diethylthiourea	2.91
6	Phenylthiourea	2.80	12	*sym*-Diphenylthiourea	2.91

studied was (Table I): *m*-tolyl $\leqslant$ *p*-tolyl $<$ *o*-tolyl $<$ phenyl $<$ diphenyl. This order is approximately satisfactory with the exception of phenyl. It would be expected that the *ortho*- and *para*-tolyl groups would contribute more to the basicity of thiourea than a phenyl group.

Stability Constants.—Values of n, the average number of reagent molecules bound to the metal, equalled four at the start of the titration in the case of each of the compounds studied with the metals copper(I), cobalt(II) and nickel(II). This indicated that at even the lowest pH limit, complete complexing had occurred. This was not too surprising, however, since a comparison of the acid dissociation constants of the various ligands indicated that with this lack of ligand basicity, the competition between the metal and proton for the ligand was not very keen, so that the metal would tend to add to the ligand immediately upon combination. Acid dissociation constants should be at least 3.5–4.0 to enable the successful determination of stepwise formation constants.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF MINING AND METALLURGY, UNIVERSITY OF BRITISH COLUMBIA]

Kinetics of the Reaction between Formic Acid and Thallium(III) in Aqueous Solution

BY H. N. HALVORSON AND J. HALPERN[1]

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Formic acid and thallic perchlorate were found to react in aqueous perchloric acid solution as follows: $Tl^{+++} + HCOOH \rightarrow Tl^{+} + 2H^{+} + CO_2$. The kinetics of this reaction were investigated between 65 and 85° and shown to be consistent with a mechanism involving the following sequence of steps (1) $Tl^{+++} + HCOOH \overset{K}{\rightleftarrows} Tl{\cdot}HCOOH^{+++}$; (2) $Tl{\cdot}HCOOH^{+++} \xrightarrow{k} Tl^{+} + 2H^{+} + CO_2$. The first step is a rapid equilibrium while the second step is rate determining. The equilibrium constant (K) and the unimolecular rate constant (k) were found to have the following values: K = 16.2 liter mole^{-1} and k = $1.0 \times 10^{13} \exp[-26600/RT]$ sec.$^{-1}$. The inhibiting effects of Cl^{-} and $SO_4^{=}$ were attributed to the fact that these ions compete with HCOOH to form complexes with Tl^{+++}. Spectrophotometric measurements were also made which provide evidence for the existence of the $Tl{\cdot}HCOOH^{+++}$ complex and quantitative support for the proposed mechanism.

Introduction

Following recent studies in this Laboratory[2] on the homogeneous reactions between molecular hydrogen and metal ions such as Cu^{++}, Ag^{+}, Hg^{++}, Hg_2^{++} and MnO_4^{-}, in aqueous solution, it seemed of interest to examine also some analogous reactions involving other molecular reducing agents whose oxidation, like that of hydrogen, involves the disruption of covalent bonds. Formic acid is one of the simplest examples of such a reducing agent and was therefore selected for study initially. Previous investigations have been reported on the reactions of formic acid with a number of oxidants in aqueous solution including the metal ions Co^{+++},[3] Hg^{++} and Hg_2^{++}.[4] In the present paper, a kinetic study of the reaction between formic acid and thallic perchlorate, in aqueous perchloric acid solution, is described.

Experimental

Reagents.—A stock solution of thallic perchlorate was prepared as follows. A solution of Analar grade thallous sulfate in aqueous perchloric acid was oxidized with sodium bromate and the resulting thallium(III) was precipitated as thallic oxide with ammonia. The precipitate was washed thoroughly, then redissolved in perchloric acid and reprecipitated with ammonia (this procedure was repeated three times to ensure removal of foreign anions). The final stock solution of thallic perchlorate, obtained by dissolving the purified oxide in perchloric acid solution, contained 0.3 M Tl^{+++}, 0.006 M Tl^{+} and 9 M $HClO_4$ and did not change over a period of four months. A second batch of thallic perchlorate solution, prepared by the same procedure, gave identical results.

Analar grade formic acid was used. Attempts to purify it further by redistillation did not alter the results. With the exception of the various perchlorate salts, which were obtained from G. F. Smith Chemical Co., all other chemicals were Baker and Adamson reagent grade products. Distilled water was used in the preparation of all solutions.

Analytical Procedures.—The Tl^{+} content of the solution was determined, following addition of HCl, by titration with standard (0.01 N) $KBrO_3$ using Brilliant Ponceau 5R (G. F. Smith Chemical Co. product) as indicator. It was established that the results were unaffected by the presence of HCOOH and of Tl^{+++}. To determine the total thallium content of the solution the Tl^{+++} was first reduced with SO_2. The excess SO_2 was then removed by boiling and the solution titrated with $KBrO_3$ as described above.

Kinetic Measurements.—The experiments were conducted in stoppered flasks immersed in a thermostated (±0.05°) water-bath. Most of the measurements were made at 74.0°. The reacting solution was prepared by mixing, in suitable proportions, standardized stock solutions (pre-heated to the reaction temperature) of the various separate components, *i.e.*, Tl^{+++}, HCOOH and $HClO_4$. To follow the reaction, samples of the solution were withdrawn

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[1] Department of Chemistry, University of British Columbia.

[2] E. Peters and J. Halpern, *J. Phys. Chem.*, **59**, 793 (1955); A. H Webster and J. Halpern, *ibid.*, **60**, 280 (1956); G. J. Korinek and J. Halpern, *ibid.*, **60**, 285 (1956); J. Halpern, *Quart. Revs.* (*London*), in press.

[3] C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 339 (1951).

[4] A. R. Topham and A. G. White, *ibid.*, 105 (1952).

periodically and analyzed for Tl^+ as described earlier. Duplicate rate measurements were generally reproducible to within ±5%. The rate was unaffected by packing the reaction flask with glass wool.

Absorption spectra were determined with a Beckman DK2 recording spectrophotometer.

Results and Discussion

Stoichiometry of the Reaction.—In the presence of HCOOH, it was found that Tl^{+++} underwent reduction to Tl^+ as shown by the rate plots in Fig. 1. This was attributed to the reaction

$$Tl^{+++} + HCOOH \longrightarrow Tl^+ + 2H^+ + CO_2 \quad (1)$$

The possibility of any other reaction in this system is very remote. Only the change in Tl^+ concentration of the solution during reaction was followed analytically. Attempts to determine the small amount of CO_2 produced were not successful. In support of the proposed stoichiometry, it was found that (a) when the initial concentration of HCOOH was greater than that of Tl^{+++}, the reduction of the latter proceeded to completion, and (b) when Tl^{+++} was initially present in excess, the final concentration of Tl^+ produced was always equal to the initial concentration of HCOOH (see Fig. 1). The stoichiometry represented by equation 1 was assumed in all the subsequent kinetic work.

Kinetics of the Reaction.—Initially a large number of experiments were conducted in which the temperature and $HClO_4$ concentration were held constant (74.0° and 3.13 *M* $HClO_4$, respectively) and the initial concentrations of Tl^{+++} and HCOOH, as well as their ratio, were varied over a wide range (the former concentration between 0.01 and 0.1 *M* and the latter between 0.01 and 2.2 *M*). In view of the bimolecular stoichiometry of the reaction it was first attempted to fit the experimental kinetic data to a second-order rate law, *i.e.*

$$\frac{dx}{dt} = k'(a - x)(b - x) \quad (2)$$

where *a* and *b* are the initial total (*i.e.*, analytical) concentrations of Tl^{+++} and HCOOH, respectively, and *x* is the Tl^+ concentration at time, *t*. As a result of these attempts, it was found that (1) the kinetics were second-order (*i.e.*, yielded a constant value of k') only at very low concentrations of both Tl^{+++} and HCOOH. (2) As the initial concentration of either or both of the reactants was increased, the kinetics deviated from second-order, the apparent value of k' becoming smaller. At the same time, a tendency was observed for k' to increase, as the reaction proceeded, during a given experiment. (3) When the concentration of one of the reactants (*i.e.*, HCOOH) was increased above 0.5 *M* the rate leveled off at a constant value (see Fig. 2). This value was found to be directly proportional to the concentration of the other reactant. (4) The rate remained unchanged when the concentrations of Tl^{+++} and HCOOH were interchanged.

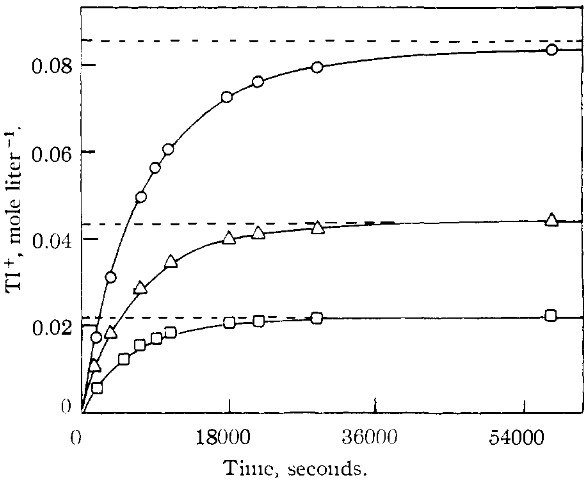

Fig. 1.—Typical rate plots at 74°: initial Tl^{+++} concn., 0.12 *M*; initial HCOOH concn. (depicted by ----), □, 0.022 *M*; △, 0.043 *M*; ○, 0.086 *M*.

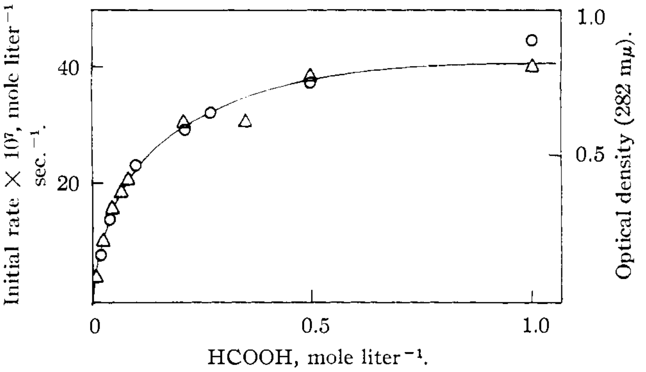

Fig. 2.—Plots of initial rate and of optical density *vs.* initial HCOOH concentration; other initial concentrations: 0.0216 *M* Tl^{+++}, 3.13 *M* $HClO_4$; △, initial rate (74°); ○, optical density (25°).

To explain these results, a mechanism is proposed which assumes that Tl^{+++} and HCOOH combine to form a relatively stable intermediate complex, $Tl{\cdot}HCOOH^{+++}$, which then undergoes unimolecular dissociation to the observed products, *i.e.*

$$Tl^{+++} + HCOOH \underset{}{\overset{K}{\rightleftharpoons}} Tl{\cdot}HCOOH^{+++} \quad (3)$$

$$Tl{\cdot}HCOOH^{+++} \xrightarrow{k} Tl^+ + 2H^+ + CO_2 \quad (4)$$

The first step is assumed to be a rapid equilibrium (governed by the equilibrium constant, *K*) while the second step (governed by the first-order rate constant, *k*) is slow and, hence, rate determining.

The concentration of the intermediate complex is thus given by

$$[Tl{\cdot}HCOOH^{+++}] = K[Tl^{+++}][HCOOH] \quad (5)$$

while the rate is given by

$$\frac{d[Tl^+]}{dt} = k[Tl{\cdot}HCOOH^{+++}] \quad (6)$$

$$= kK[Tl^{+++}][HCOOH] \quad (7)$$

where $[Tl^{+++}]$ and [HCOOH] represent the actual concentrations of free (*i.e.*, uncomplexed) Tl^{+++} and HCOOH in the solution.

Through appropriate substitutions involving the following conditions

$$a = [Tl^{+++}] + [Tl{\cdot}HCOOH^{+++}] + x \quad (8)$$

and

$$b = [HCOOH] + [Tl{\cdot}HCOOH^{+++}] + x \quad (9)$$

equation 7 reduces to

$$\frac{dx}{dt} = \frac{k[K(a + b - 2x) + 1 - \sqrt{K^2(a - b)^2 + 2K(a + b - 2x) + 1}]}{2K} \qquad (10)$$

where a, b and x have the same meaning as in eq. 2. Integration of eq. 10 yields

$$(1/A) \log [(F_x + A)/(F_x - A)] - \log (F_x^2 - A^2) = kt/2.3 + C \qquad (11)$$

where

$$F_x = \sqrt{K^2(a - b)^2 + 2K(a + b - 2x) + 1} - 1 \qquad (12)$$

and

$$A = K(a - b) \qquad (13)$$

In the special case where the initial total concentrations of Tl^{+++} and HCOOH are equal, *i.e.*, $a = b$, the integrated rate equation has the form

$$1/G_x - 2.3 \log G_x = kt/2 + C \qquad (14)$$

where

$$G_x = \sqrt{4K(a - x) + 1} - 1 \qquad (15)$$

and C is the integration constant in each case.

Using a value of 16.2 liter mole^{-1} for K (estimated in the first instance by extrapolating the experimental kinetic data to high dilutions where equations 2 and 7 become equivalent, *i.e.*, $k' = kK$) the functions corresponding to the left-hand sides of equations 11 and 14 were calculated and plotted against t, for a number of experiments, in Figs. 3 and 4, respectively. Excellent agreement with the predicted behavior is observed, *i.e.*, in each case the results conform to a series of parallel linear plots. The slopes of these plots yield a consistent value of 1.7×10^{-4} sec.$^{-1}$ for k (at 74.0°).

Spectrophotometric Evidence for the Intermediate Complex.—The relatively high value of K (*i.e.*, 16.2 liter mole^{-1}) deduced above from the kinetic results, suggested that the intermediate complex was present in appreciable concentrations and hence that it might be possible to detect its presence spectrophotometrically. Accordingly, the ultraviolet absorption spectra of a series of 0.0216 M Tl^{+++} solutions containing different concentrations (between 0 and 1.0 M) of HCOOH were determined and are reproduced in Fig. 5. It is seen that while HCOOH itself does not absorb appreciably at wave lengths above 260 mμ, its presence markedly increases the absorption of Tl^{+++} in this region. It seems reasonable to conclude that this increased absorption is due to a complex formed between Tl^{+++} and HCOOH. In this connection it seems particularly significant that the curve depicting the optical density (measured at 282 mμ and corrected for the small absorption of the uncomplexed Tl^{+++} in this region) has the same shape as that for the rate. Both these curves are plotted in Fig. 2, using suitably scaled coördinates to facilitate comparison. This provides convincing support for the conclusion that both the rate and the optical absorption are determined by the same complex.

Temperature Dependence of K and k.—In connection with the data in Fig. 2, it is als of interest to note that while the rate measurements were made at 74°, the optical absorption (because of experimental limitations) was measured only at 25°. If the interpretation given above, *i.e.*, that each of these properties reflects the variation of the concentration of the complex $Tl{\cdot}HCOOH^{+++}$ is correct, then the shape of the curve depicting its dependence on the HCOOH concentration should depend on the value of K. The similarity of the shapes of the two plots in Fig. 2 therefore suggests that the temperature coefficient of K is small.

Support for this suggestion is also derived from measurements of the temperature dependence of the rate. Two series of kinetic experiments were made over the temperature range 65° to 85°. In each series the initial Tl^{+++} concentration was 0.0216 M while the HCOOH concentrations were 0.0216 and 0.50 M respectively. The apparent activation energies, based on the initial rates were found to be 26.1 and 25.6 kcal./mole, respectively, for the two series. Evidence previously noted suggests that at the lower HCOOH concentration, only a small proportion of the HCOOH and Tl^{+++} is complexed while at the higher concentration nearly all the Tl^{+++} is in the form of the $Tl{\cdot}HCOOH^{+++}$ complex. From a consideration of equations 6 and 7, it is then apparent that in the first case the rate tends to be proportional to kK, while in the latter case it is proportional to k. The fact that both series of rate measurements yield essentially the same apparent activation energy, thus affords further indication that K is not appreciably temperature dependent. Furthermore, it was found that, using a constant value of K (*i.e.*, the value of 16.2 liter mole^{-1} determined for 74°), good linear plots were obtained when the function $-2.3 \log G_x + 1/G_x$ was plotted against t for a series of experiments at different temperatures. Values of k, calculated from the slopes of these plots by means of equation 11, gave a good Arrhenius plot, fitted by the equation

$$k = 1.0 \times 10^{13} \exp[-26600/RT] \text{ sec.}^{-1} \qquad (16)$$

The value of the frequency factor thus determined (corresponding to an activation entropy of -1.3 e.u.) is normal for a unimolecular reaction and is thus consistent with the proposed mechanism.

Effect of Solution Composition.—All the experiments described above were made with solutions containing 3.13 M $HClO_4$ and no added salts. The relatively high acid concentration was selected to minimize complications due to hydrolysis of Tl^{+++} and to dissociation of HCOOH. Thus available data[5,6] indicate that at 3.13 M H^+ only about 2% of the Tl^{+++} is hydrolyzed while less than 0.01% of the HCOOH is dissociated. Hence it was assumed that contributions to the reaction from species other than Tl^{+++} and HCOOH (*i.e.*, such as $TlOH^{++}$ and $HCOO^-$) were negligible.

Results obtained on varying the $HClO_4$ concentration are given in Table I and support this interpretation. Thus it is seen that the rate is relatively insensitive to variations in the $HClO_4$ concentration above 3 M but increases at lower concentrations. This increase is attributed to hydrolysis of the

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(5) G. Biedermann, *Arkiv Kemi*, **5**, 441 (1953).

(6) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952, p. 184.

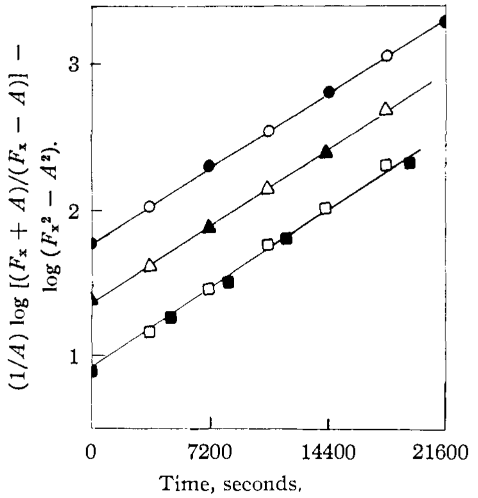

Fig. 3.—Kinetic plots at 74°, 3.13 M HClO$_4$; initial total concn. (M) of Tl^{+++} and HCOOH, respectively: ○, 0.03, 0.0216; ●, 0.0216, 0.03; △, 0.05, 0.0216; ▲, 0.0216, 0.05; □, 0.095, 0.0216; ■, 0.0216, 0.095.

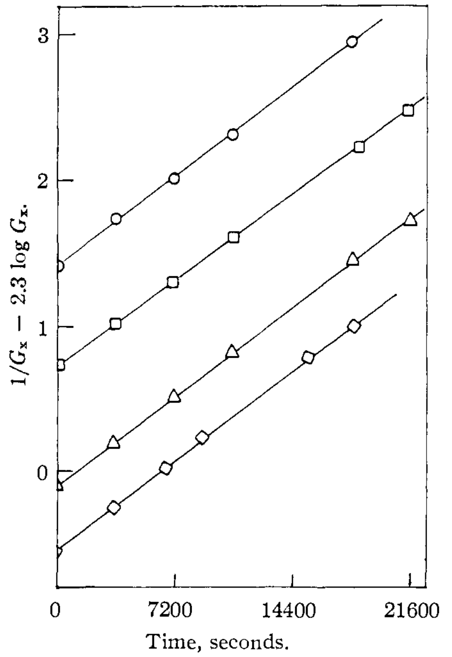

Fig. 4.—Kinetic plots at 74°, 3.13 M HClO$_4$; initial concn. (M) of Tl^{+++} and HCOOH (equal): ○, 0.0216; □, 0.03; △, 0.05; ◇, 0.07.

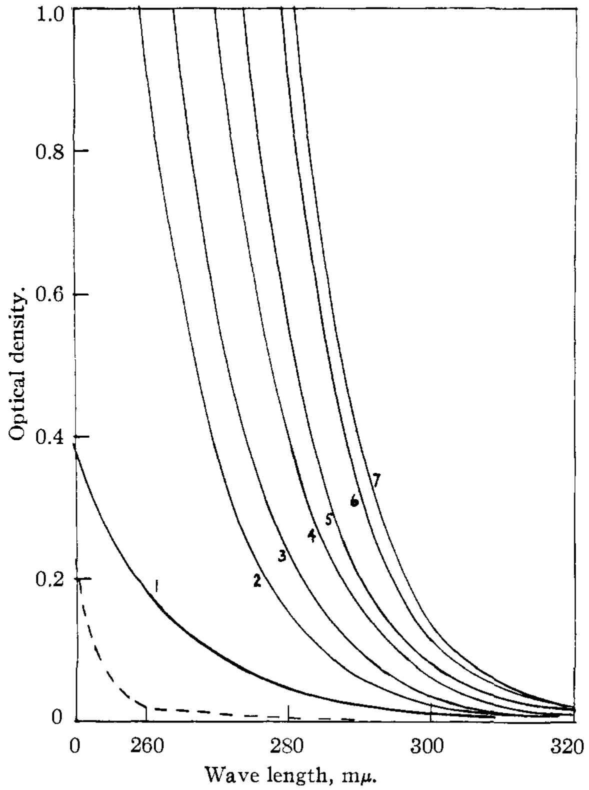

Fig. 5.—Absorption spectra at 25° of 3.13 M HClO$_4$ solutions containing 0.0216 M Tl^{+++} and various amounts of HCOOH; HCOOH concn. (M): 1, 0.0; 2, 0.01; 3, 0.02; 4, 0.04; 5, 0.1; 6, 0.5; 7, 1.0, (---- denotes absorption of 1 M HCOOH in absence of Tl^{+++}).

Tl^{+++}, *i.e.*, to increased contributions to the reaction from the species TlOH^{++}, possibly reflecting its greater tendency to complex with HCOOH or the greater reactivity of the resulting complex.

Also listed in Table I are the results of a number of experiments in which various salts were added to the solution. Perchlorate salts such as NaClO$_4$, Mg(ClO$_4$)$_2$, Co(ClO$_4$)$_2$, Cu(ClO$_4$)$_2$ and AgClO$_4$ were apparently without appreciable effect on the rate (this is of interest in view of the marked catalytic effects of Cu^{++} and Ag^{+} on the reactions of H$_2$ in aqueous solution[2]). On the other hand, the addition of chlorides, *i.e.*, NaCl and HCl resulted in a drastic reduction in the rate. This is attributed to the formation of the very stable TlCl^{++} complex. Thus the value determined above for K (16.2 liter mole^{-1}), coupled with available data[7] for the dissociation constant for TlCl^{++} ($\approx 8 \times 10^{-9}$ mole liter^{-1}), suggest that the equilibrium constant of the reaction

$$\text{Tl·HCOOH}^{+++} + \text{Cl}^- \rightleftarrows \text{TlCl}^{++} + \text{HCOOH} \quad (17)$$

TABLE I

EFFECT OF SOLUTION COMPOSITION ON THE RATE AT 74°

Initial concentrations of HCOOH and Tl(ClO$_4$)$_3$ = 0.0216 M

[HClO$_4$], mole/l.	Added salt	Initial rate (× 10^7), mole/l. sec.
1.01	....	15.8
1.65	....	12.0
2.60	....	9.3
3.13	....	8.4
4.00	....	7.3
5.00	....	7.6
3.13	2 M NaClO$_4$	8.5
3.13	0.005 M HCl	6.3
3.13	0.01 M HCl	5.4
3.13	0.022 M HCl	1.6
3.13	1.0 M NaCl	0.0
3.13	1.0 M Na$_2$SO$_4$	3.2
3.13	0.02 M Tl$_2$SO$_4$	7.3
3.13	.1 M Co(ClO$_4$)$_2$	8.3
3.13	.1 M AgClO$_4$	7.6
3.13	.1 M Cu(ClO$_4$)$_2$	7.6
3.13	.1 M Mg(ClO$_4$)$_2$	8.2

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(7) R. Benoit, *Bull. soc. chim. France*, 518 (1949).

is about 10^7, *i.e.*, that the equilibrium lies very far to the right. In keeping with this it is found that the fraction by which the reaction rate is reduced is approximately equal to the ratio of the total concentrations of Cl^- to Tl^{+++} in the solution. The explanation for the inhibition of the reaction by $SO_4^=$, which is less marked than for Cl^-, is probably analogous.

Conclusions

Kinetic evidence has been provided in support of the suggestion that the reaction between Tl^{+++} and HCOOH in aqueous solution proceeds *via* the formation of a relatively stable intermediate complex, $Tl\cdot HCOOH^{+++}$, whose unimolecular rearrangement is the rate-determining step. All the kinetic data are apparently consistent with this mechanism. The existence of the proposed complex is also supported by spectrophotometric measurements.

Although the occurrence of complexes of metal ions such as Tl^{+++} with anions such as OH^-, Cl^-, $HCOO^-$, CH_3COO^-, etc., is fairly widespread, the formation of a complex with an undissociated acid molecule is unusual (that the complex involved is $Tl\cdot HCOOH^{+++}$ rather than $Tl\cdot HCOO^{++}$ must be concluded from the fact that its concentration is apparently independent of *p*H in a region where Tl^{+++} is largely unhydrolyzed and HCOOH is largely undissociated). Chemical considerations, coupled with its spectral characteristics, suggest that the complex is of the charge transfer type.[8]

Evidence has been presented to indicate that the formation of the complex is thermoneutral. This means that for reaction (3), $\Delta H° = 0$ and hence that $\Delta S° = -\Delta F°/T = R \ln K$. Substituting the experimental value of K (*i.e.*, 16.2 liter mole^{-1}) yields a value of 5.6 e.u. for $\Delta S°$. The positive entropy change presumably reflects the liberation of one or more water molecules from the hydration shell of Tl^{+++} when the latter forms a complex with HCOOH.

The reactions of HCOOH with other oxidizing metal ions, such as Co^{+++}, Hg^{++} and Hg_2^{++} have been postulated to occur through a simple bimolecular rate-determining step in which a single electron is transferred from HCOOH (or $HCOO^-$) to the metal ion resulting in the formation of an intermediate HCOO· radical.[3,4] There is no evidence that such an intermediate is formed in the present reaction and (in view of the instability of Tl^{++}) it seems more reasonable to conclude that the $Tl\cdot HCOOH^{+++}$ complex rearranges directly to the products (*i.e.*, *via* a two-electron transfer mechanism). Conversely there is no direct evidence that the mechanism proposed in the present case applies to the reactions of HCOOH with any of the other metals ions. In none of the other cases was any appreciable deviation from second-order kinetics reported which might suggest the accumulation of a complex between the reactants. Possibly the kinetic measurements were not sufficiently accurate to detect such a deviation or the concentrations of the complexes were much lower than in the present case. The only anomalous feature of the kinetics of these reactions, which might possibly be accounted for by the formation of an intermediate complex, is that the frequency factors which were reported in each case, were abnormally high (10^{15}–10^{18} liter mole^{-1}sec.$^{-1}$) for a simple bimolecular reaction.[3,4]

It is of some interest to compare the present reaction of HCOOH with some of the homogeneous reactions of H_2 in aqueous solution. In general, the reactions of the latter are much slower; thus no homogeneous reaction between Tl^{+++} and H_2 has been detected up to 100°. In the case of some of the other homogeneous reactions of H_2 that have been studied, *i.e.*, with Cu^{++}, Hg^{++}, Hg_2^{++} and MnO_4^-, the second-order kinetics suggest, in each case, a simple bimolecular rate-determining step in which a two-electron transfer (or possibly a H^- ion transfer) occurs from H_2 to the oxidant. In the present case it seems probable that such a transfer, between HCOOH and Tl^{+++}, occurs intramolecularly, *i.e.*, within the $Tl\cdot HCOOH^{+++}$ complex. The reaction of H_2 with Cu^{++} has been postulated[9] to occur *via* the intermediate, CuH^+. However, in no case is there any evidence for the formation of a stable intermediate complex involving an H_2 molecule (*i.e.*, analogous to $Tl\cdot HCOOH^{+++}$). Probably this reflects the fact that the polarizability of H_2 is much smaller and its ionization potential greater, than those of HCOOH.

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[8] L. E. Orgel, *Quart. Revs.* (*London*), **8**, 422 (1954).

[9] J. Halpern, E. R. Macgregor and E. Peters, *J. Phys. Chem.*, **60**, 1455 (1956).