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Kinetics of Thallium(I)–Triiodide Complexation in Aqueous Perchloric Acid

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Abstract: The specific rate constant for the formation of the 1:1 thallium(I)–triiodide complex in aqueous perchloric acid (10^{-2} *M*) has been measured over the temperature range 5–45° using the stopped-flow technique. The reaction is first order in both ions when Tl^+ is kept in large excess over the I_3^- ion concentration, at least 200:1. Formation of higher complexes complicates the kinetic interpretation when the ion concentration ratio is reversed. Consequently, rate studies were made under pseudo-first-order experimental conditions. The resultant second-order rate constant k_3 is $(1.75 \pm 0.03) \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at 25° which is comparatively low for substitution rates into univalent ions and may indicate ligand dependence in the rate-determining step. Activation parameters for the reaction are $\Delta H^\ddagger = 7.24$ kcal mol^{-1} and $\Delta S^\ddagger = -14.8$ cal deg^{-1} mol^{-1} which are large for univalent ion interactions and may indicate drastic solvent reorganization around Tl(I) in forming the activated complex.

The equilibrium reaction in which iodide ion and the iodine molecule associate to form the triiodide complex ion has been the subject of numerous investigations in a variety of solvents.[2] Anomalies observed when the data were treated in terms of only the one to one association, have, for the most part, been rationalized in terms of higher associations,[3,4] *e.g.*, to I_5^- and I_6^{2-}. From recent laser resonance Raman spectroscopy,[5] equilibrium,[6] and calorimetric[7] investigations, there is evidence in favor of a cation–triiodide association reaction which could be offered as an alternative reaction to polyiodide formations. The evidence is especially convincing when Tl(I) is the counterion. We report here what we believe to be the first kinetic study of the complexation of Tl(I), although the two-electron transfer process Tl(I) $\rightleftharpoons$ Tl(III) has been the subject of extensive study and much controversy for many years.[8]

Experimental Section

Solutions were prepared using redistilled, deionized water and analytical grade thallium nitrate (Matheson Coleman and Bell Co., Inc.), potassium iodide (Matheson Coleman, and Bell Co., Inc.), and resublimed iodine (Allied Chemical Co.). To supress the hydrolysis of iodine, all solutions contained 10^{-2} *M* perchloric acid. All other solute concentrations were 10^{-3} *M* or less so the studies were made at essentially constant ionic strength. Potassium iodide was kept at least five times in excess of iodine, solutions being prepared immediately prior to the kinetic studies.

Kinetic experiments were done on a Durrum-Gibson stopped-flow instrument at 5, 15, 25, 35, and 45°, all temperatures being maintained to within ±0.2°. In the presence of thallium(I) ion the spectrum of triiodide solutions shows a new absorption band[7] with a maximum optical density at 395 nm. The kinetics of the reaction were followed at two wavelengths, at 395 and at 360 nm, the wavelength of maximum absorption of triiodide. Both analyses gave the same kinetic result and as such demonstrated the one to one correspondence between the loss of triiodide and the production of the TlI_3 complex.

Results

The compound with the stoichiometric formula TlI_3 is known to be thallium(I) triiodide, and not thallium(III) iodide, because of an internal oxidation–reduction reaction. At pH 2, no complications from the hydrolysis of Tl(I) arise, and the hydrolysis of iodine is suppressed. The equilibrium reactions which exist in solution are therefore

$$I_2 + I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I_3^- \tag{1}$$

and the complexation of thallium(I),

$$Tl^+ + I_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} TlI_3 \tag{2}$$

Other possible complexes[9] such as $TlNO_3$ and $TlI_x^{(x-1)-}$ have been shown to be unimportant provided the metal ion was kept in large excess.[6] A kinetic study of reaction 1 was reported by Sutin, *et al.*,[10] using the laser-Raman temperature jump technique, and the reaction is too rapid to be that observed in the stopped-flow experiments: $k_1 = 6.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, $k_2 = 8.5 \times 10^6\ \text{sec}^{-1}$. A steady state kinetic analysis of the successive reactions 1 and 2 shows that the observed rate constant, k_{obsd}, is equal to k_3. Equilibrium

Table I. Concentration Data: Initial and Equilibrium Conditions

Equilibrium constants[a]	5°	15°	25°	35°	45°
K_1	1000	933	760	596	425
K_c	505	625	730	746	678

10^4C_I, m	10^5C_2, m	10^3C_M, m	$10^7[I_3^-]$, m (initial)	$10^7[I_3^-]$, m (final)	$10^7[TlI_3]$, m (final)
		5°			
0.501	1.034	0.501	4.885	4.817	1.219
0.501	1.034	1.002	4.885	4.751	2.404
0.501	1.034	2.004	4.885	4.624	4.679
1.002	2.068	1.002	18.509	17.582	8.890
1.002	2.068	2.004	18.509	16.753	16.942
		15°			
0.501	1.034	0.501	4.575	4.501	1.409
0.501	1.034	1.002	4.575	4.430	2.774
0.501	1.034	2.004	4.575	4.294	5.378
1.002	2.068	1.002	17.391	16.386	10.252
1.002	2.068	2.004	17.391	15.503	19.400
		25°			
0.501	1.034	0.501	3.763	3.705	1.355
0.501	1.034	1.002	3.763	3.648	2.668
0.501	1.034	2.004	3.763	3.540	5.179
1.002	2.068	1.002	14.431	13.618	9.952
1.002	2.068	2.004	14.431	12.901	18.851
		35°			
0.506	1.023	0.503	2.977	2.939	1.102
0.506	1.023	1.006	2.977	2.902	2.177
0.506	1.023	2.012	2.977	2.831	4.248
1.012	2.045	1.006	11.511	10.968	8.223
1.012	2.045	2.012	11.511	10.479	15.713
		45°			
1.012	2.045	1.006	8.368	8.101	5.522
1.012	2.045	2.012	8.368	7.853	10.704

[a] Data from unpublished work, J. D. Miller, Ph.D. Dissertation, Oklahoma State University, May 1973.

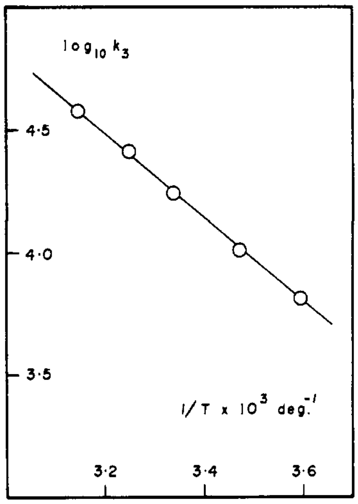

Figure 1. The Arrhenius plot, log k_3 *vs.* $1/T$ (degree K)$^{-1}$, for the complexation of Tl^+ by I_3^-.

Table II. Kinetic Results for TlI_3 Complex Formation

Temp, °C	Initial slope (10^5 M/sec)	k_3' (sec^{-1})	$10^{-4}k_3$ (M^{-1} sec^{-1})	Mean $10^{-4}k_3$
5	0.148	1.74	0.35	
	0.235	4.82	0.48	
	0.698	14.28	0.71	
	1.277	6.90	0.69	
	3.746	20.24	1.01	0.65 ± 0.2
15	0.169	3.69	0.74	
	0.402	8.78	0.88	
	0.957	20.92	1.04	
	1.755	10.09	1.01	
	4.179	24.03	1.19	0.97 ± 0.13
25	0.327	8.68	1.73	
	0.646	17.18	1.71	
	1.355	36.01	1.80	
	2.482	17.20	1.72	
	5.135	35.58	1.78	1.75 ± 0.03
35	0.392	13.18	2.62	
	0.757	25.42	2.53	
	1.564	52.52	2.61	
	2.898	25.18	2.50	
	6.166	53.57	2.62	2.58 ± 0.05
45	3.111	37.18	3.70	
	6.379	76.23	3.79	3.75

constants for reaction 2 measured spectrophotometrically are ≥500 over the temperature range investigated, so the contribution from the backward reaction in eq 2 can be ignored in the kinetic analysis.

The voltage change observed in the oscilloscope trace on mixing the reactants and stopping the flow is proportional to a complex change in optical density. Both species I_3^- and TlI_3 absorb at both wavelengths, and as the reaction proceeds the optical density, say at 395 nm, increases as TlI_3 is formed in eq 2, decreases as I_3^- is consumed in eq 2, and increases as I_3^- is produced by the concomitant displacement of eq 1 to the right. To simplify the interpretation of the kinetic curves, experimental conditions were chosen such that changes in the triiodide concentration were very small; thus the voltage change was almost exactly proportional to the change in $[TlI_3]$ alone. At 395 nm the molar extinction coefficient of the TlI_3 is almost twice that of I_3^-. By working at low total triiodide concentrations and at $[Tl^+]$ 20–1000 times greater than $[I_3^-]$, the change in $[TlI_3]$ was at least ten times the change in $[I_3^-]$, and the error in the approximate proportionality was at worst 5%. The very large excesses of Tl^+ over I_3^- also served to reduce the form of the rate equation to pseudo-first-order kinetics

$$\frac{d[TlI_3]}{dt} = k_3[Tl^+][I_3^-] = k_3'[I_3^-] \tag{3}$$

since the $[Tl^+]$ is virtually constant during any one experiment.

Initial reactant concentrations were prepared by weight. Equilibrium concentrations were determined from an iterative calculation using the equations for the equilibrium constants for reactions 1 and 2, *i.e.*

$$K_1 = \frac{[I_3^-]}{[I_2][I^-]} \tag{4}$$

and

$$K_c = K_2\gamma_1^2 = \frac{[TlI_3]}{[Tl^+][I_3^-]} \tag{5}$$

and the mass balance equations for total iodide, C_1, total iodine, C_2, and total metal, C_M. Values for K_1 and the conditional constant K_c, referring to a medium of 10^{-2} $HClO_4$, were determined spectrophotometrically and are given in Table I. Our values for K_1 at 5, 25, and 45° are in excellent agreement with previous literature values.[3] A separate description of the thermodynamic studies is in preparation.

In the evaluation of the pseudo-first-order rate constants k_3' initial slopes were measured directly from photographs. Pertinent concentration data are presented in Table I, and the rate constants k_3', equal to the initial slope divided by the initial triiodide concentration, and k_3 are given in Table II. The activation parameters at 25° are given in Table III.

Table III. Activation Parameters for TlI_3 Complexation at 25°

	Complexation	Dissociation
k_3	$1.75 \times 10^4\ M^{-1}\ sec^{-1}$	
k_{-3}		$24\ sec^{-1}$
$\Delta G^\ddagger$	$11.65\ kcal\ mol^{-1}$	$15.5\ kcal\ mol^{-1}$
$\Delta H^\ddagger$	$7.24\ kcal\ mol^{-1}$	$4.5\ kcal\ mol^{-1}$
$\Delta S^\ddagger$	$-14.8\ cal\ deg^{-1}\ mol^{-1}$	$-30.4\ cal\ deg^{-1}\ mol^{-1}$

Discussion

For K^+, an ion of approximately the same size as Tl^+, the specific rate constant for the formation of the nitrilotriacetic acid complex[11] is $2 \times 10^8\ M^{-1}\ sec^{-1}$. In comparison the rate of complex formation of thallium(I) triiodide is very slow. Two possible explanations which could account for this difference are (1) substitution rates are ligand dependent, a premise which could be tested by examining a variety of ligands and (2) from thermodynamic studies Tl(I) ion is believed to bond covalently with a variety of ligands.[9,12] This latter specific interaction could conceivably be accompanied by drastic reorganization of the first coordination sphere, perhaps even a coordination number change.

The observed rate of complex formation is rapid compared to the rate of electron transfer from Tl^+ to Tl^{3+}, *e.g.*, $7.0 \times 10^{-5}\ M^{-1}\ sec^{-1}$ in 3 *M* $HClO_4$.[8] If electron transfer proceeds by an inner-sphere mechanism, some other step, besides substitution into the first coordination sphere of either ion, is rate determining. The solvent exchange rate[13] on Tl^{3+} is $3 \times 10^9\ sec^{-1}$.

As evidence in support of the result from the present work we would cite the somewhat tenuous comparison with the rate of oxidation of Tl^+ by bromine[14] according to the equation

$$Tl^+ + Br_2 \rightleftharpoons TlBr_2^+ \qquad (6)$$

Although nominally the addition of a bromine molecule to Tl^+, the reaction is indeed a two-electron redox reaction. If electron transfer is rapid compared to substitution, and the substitution is mechanistically similar to I_3^- substitution, the rate of reaction would be slightly less for bromine, an uncharged molecule, than it is for the univalent triiodide ion. The value reported for reaction 6 is $0.72 \times 10^4\ M^{-1}\ sec^{-1}$.

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Pulsed ^{13}C Fourier Transform Nuclear Magnetic Resonance Spectra of Monohalo-Substituted Cyclohexanes at Low Temperatures[1]

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Abstract: The low-temperature pulsed ^{13}C FT nmr spectra of a series of monohalocyclohexanes have been measured. The chemical shift substituent parameters for both the isomers (*i.e.*, equatorial and axial) have been derived. The integral peak intensity data are used for the conformational energy ΔG_T determination. The energies proved to be close to those previously reported in the literature. Carbon chemical shifts at ambient temperatures are applied to determine the conformational contents by employing the substituent parameters. Various ^{13}C-^{19}F splittings have been found in the case of fluorocyclohexane, and the vicinal ^{13}C-^{19}F coupling constants have been found to be sensitive to dihedral angles. The substituents Cl, Br, I produce a strong γ effect (*ca.* 6 ppm). For fluorine, the γ effect is substantially lower (*ca.* 3.6 ppm).

Monosubstituted cyclohexanes are classical and well documented examples of conformationally flexible systems. The main interest of most studies[2] is concerned with the conformational energy at temperature T, $\Delta G°_T$ equal to $G_T(ax) - G_T(eq)$, where $G_T(ax)$ and $G_T(eq)$ are the free energies of the axial and equatorial conformers, respectively.

Previous investigations of conformational equilibria in substituted cyclohexanes used various techniques, proton magnetic resonance spectroscopy included. In particular, Jensen, *et al.*,[2c,e] found some of the conformational energies by using very careful measurements of integral intensities in the pmr spectra at low temperatures (*ca.* −90°). Two meth-