as isoelectronic $Cr(CO)_5L$ derivatives, where k_2 is significantly greater than k_1. However in the rhenium phosphine analogs k_2 is considerably larger than k_1, the difference being on the order of that observed in the neutral isoelectronic group 6 derivatives, e.g., $W(CO)_5PPh_3$.[4]

These observations taken together may indeed be indicative of direct donation of electron density into the π^* orbitals of the equatorial CO ligands by phosphorus ligands in $M(CO)_5L^+$ derivatives.[25,26] It would be expected that in going from Cr to Mn the direct donation would increase, whereas in going from Mn to Re the direct donation would decrease.[27]

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Registry No. $[CH_3CNMn(CO)_5][PF_6]$, 55029-96-4; $[(CH_3)_2PhPMn(CO)_5][BF_4]$, 54039-48-4; $[(CH_3)_2PhPMn(CO)_5][PF_6]$, 54039-52-0; $[Ph_3PMn(CO)_5][BF_4]$, 54039-46-2; $[Ph_3PMn(CO)_5][PF_6]$, 54039-57-5; $[(PhO)_3PMn(CO)_5][BF_4]$, 54039-50-8; $[(p\text{-}MeC_6H_4)_3PMn(CO)_5][PF_6]$, 54039-59-7; $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Mn(CO)_5\}\{PF_6\}$, 54039-56-4; $[C_5H_5NMn(CO)_5][PF_6]$, 54039-54-2; $[CH_3CNRe(CO)_5][PF_6]$, 55057-83-5; $[(CH_3)_2PhPRe(CO)_5][PF_6]$, 55057-85-7; $[(p\text{-}MeC_6H_4)_3PRe(CO)_5][PF_6]$, 55029-93-1; $[(C_5H_5N)_2(CH_3CN)Mn(CO)_3][PF_6]$, 55029-80-6; $[(C_5H_5N)_3Mn(CO)_3][PF_6]$, 55029-82-8; $[(CH_3CN)_3Mn(CO)_3][PF_6]$, 55029-84-0; $[(CH_3CN)(diphos)Mn(CO)_3][PF_6]$, 55029-86-2; $Mn(CO)_3((CH_3)_2CO)_3^+$, 55029-87-3; $FMn(CO)_3(PPh_3)_2$, 55029-88-4; *cis*-$((CH_3)_2PPh)Mn(CO)_4C(=O)NHCH_3$, 54064-21-0; *cis*-$(Ph_3P)Mn(CO)_4C(=O)NHCH_3$, 55029-89-5; *cis*-$(diphos)Mn(CO)_4C(=O)NHCH_3$, 55029-90-8; *cis*-$((p\text{-}MeC_6H_4)_3P)Mn(CO)_4C(=O)NHCH_3$, 55029-91-9; *cis*-$(CH_3NH_2)Mn(CO)_4C(=O)NHCH_3$, 18973-77-8; $[Ph_3PMn(CO)_4]_2$, 10170-70-4; $[(PhO)_3PMn(CO)_4]_2$, 15529-62-1; $[(CH_3)_2PhPMn(CO)_4]_2$, 55029-78-2; $Mn_2(CO)_{10}$, 10170-69-1; Ph_3P, 603-35-0; $(PhO)_3P$, 101-02-0; $Re_2(CO)_{10}$, 14285-68-8; C_5H_5N, 110-86-1; CH_3CN, 75-05-8; CH_3NH_2, 74-89-5.

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Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Kinetics of Complexation of Silver(I) with Thiosulfate Ion in Aqueous Solution

MICHAEL M. FARROW, NEIL PURDIE,[1] and EDWARD M. EYRING*

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A specific rate constant for the rapid complexation of Ag^+ ion by thiosulfate ion in aqueous solution was determined using the recently developed laser optical–acoustic technique for sound absorption measurements. In aqueous solution the predominant complexed species is the 1:2 ion $Ag(S_2O_3)_2^{3-}$. Over the 15–230-MHz frequency range of the measurements two relaxations were observed. Both relaxations have been attributed to the stepwise mutual approach of $AgS_2O_3^-$ and $S_2O_3^{2-}$, with the elimination of coordinated water to form the 1:2 complex ion, i.e., to the second association step in the complete reaction. At 25° the specific rate constant k_3 for this association reaction is $3.5 \times 10^9\ M^{-1}\ sec^{-1}$. The result is compared with the theoretical value assuming diffusion control, with the theoretical value for the preceding step, and with a previously published value for Ag^+ complexation by *o*-phenanthroline.

Introduction

The kinetics of metal complexation reactions in which the central metal is a univalent ion have attracted comparatively little attention[2a] until the recent appearance of a flurry of kinetic studies of alkali metal ion complexation by antibiotics, crown ethers, and related ligands.[2b] Apart from Tl^+ complexation,[3] which is a relatively slow process, the rates of univalent ion complexation reactions are very rapid requiring access to sophisticated relaxation kinetic methods. Interpreting the mechanisms of chelation processes involving multidentate ligands with multivalent ions has been the objective of the great majority of the kinetic studies of metal complexation reactions.[2a,4] Although we do not propose a systematic study of univalent ion complexation reactions, these should not be excluded entirely from such investigations.

So far as its first coordination sphere is concerned, Ag^+ is generally believed to be predominantly two-coordinate because of the sp-hybridized coordination orbitals on the ion.[4] Thus,

Table I. Experimental Frequencies and Excess Sound Absorption Data as $(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$

$[Ag^+] = 0.150\ F$, $[S_2O_3^{2-}] = 0.50\ F$		$[Ag^+] = 0.200\ F$, $[S_2O_3^{2-}] = 0.50\ F$		$[Ag^+] = 0.250\ F$, $[S_2O_3^{2-}] = 0.50\ F$		$[Ag^+] = 0.387\ F$, $[S_2O_3^{2-}] = 0.50\ F$		$[Ag^+] = 0.310\ F$, $[S_2O_3^{2-}] = 0.40\ F$	
$10^4(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$, Np	f, MHz	$10^4(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$, Np	f, MHz	$10^4(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$, Np	f, MHz	$10^4(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$, Np	f, MHz	$10^4(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$, Np	f, MHz
4.480	14.85	6.19	14.85	11.17	15.03	14.97	15.00	11.56	25.08
3.88	25.22	6.07	15.03	9.06	14.85	17.99	25.11	16.62	35.15
4.85	35.00	6.24	25.22	12.0	25.01	20.63	35.04	17.23	45.20
5.42	45.12	6.37	25.12	11.27	25.22	30.59	55.17	19.17	55.26
6.53	55.14	8.18	35.09	15.74	35.08	35.78	75.31	23.28	65.21
8.72	65.21	8.93	35.10	14.15	35.09	37.84	95.35	21.39	75.32
8.08	75.25	10.86	45.12	18.03	45.17	44.70	115.48	26.74	85.30
9.91	95.28	12.53	55.19	17.75	45.12	49.90	135.60	24.00	95.33
10.43	105.35	12.60	55.20	20.07	55.12	55.00	175.65	29.81	105.39
11.56	115.36	12.61	65.22	20.50	55.19	59.68	215.92	34.63	135.45
12.77	125.44	13.41	65.23	22.39	65.17	57.35	235.00	36.28	155.54
12.48	135.49	14.36	75.24	22.40	65.22			38.61	175.52
		15.40	75.31	24.78	75.20			38.18	195.20
		17.20	85.30	23.84	75.24			39.25	195.48
		17.61	95.32	27.36	85.20				
		17.88	105.35	26.30	85.28				
		19.28	105.36	28.67	95.20				
		18.38	115.37	28.65	95.28				
		19.48	115.38	30.80	105.36				
		20.69	125.44	33.45	115.36				
		18.76	135.49	32.50	145.54				
		22.79	145.54						
		21.79	155.46						
		22.37	165.59						
		23.66	175.63						
		19.80	185.71						

Table II. Relaxation Parameters from Computer-Simulated Double-Relaxation Analysis[a]

m, F	s, F	f_1, MHz	$10^4(\alpha_{\text{chem}}\lambda)$, Np	f_2, MHz	$10^4(\alpha_{\text{chem}}\lambda)$, Np	Rms × 10^5 [b]
0.387	0.50	264 ± 6	58.2	17.2 ± 2.5	8.1	5.4
0.310	0.40	229 ± 6	38.5	12.2 ± 2.5	5.7	2.9
0.250	0.50	181 ± 8	34.0	3.2 ± 5.0	10.9	1.7
0.200	0.50	189 ± 10	21.4	2.0 ± 3.0	9.1	3.1
0.150	0.50	277 ± 25	15.3	7.1 ± 5.0	3.2	2.4

[a] All symbols as defined in text. [b] Root-mean-square deviation.

chelation is not a possibility except under very special requirements in the ligand structure. In choosing a ligand for this study, we sought one which formed a stable 1:1 complex as well as a stable 1:2 complex so that the rate of second substitution, free from the complicating features of ring closure, could be contrasted with that for first substitution. The thiosulfato complexes of silver meet these requirements, and this particular system is of further interest because of its utility in photographic fixing processes.

Experimental Section

Ultrasonic absorption measurements were made at 25 ± 0.1° over the frequency range 15–230 MHz using the laser optical–acoustic technique recently developed in this laboratory.[5] The argon ion laser was operated at the 514.5-nm green line, and the single acoustic transducer was a gold-plated 5-MHz fundamental frequency, X-cut quartz crystal which could be operated successfully at odd harmonics over this frequency range. Excess or chemical absorptions were obtained by difference from successive measurements on sodium thiosulfate–sodium chloride (background) and sodium thiosulfate–silver chloride solutions of equivalent concentrations.

Solutions were prepared using deionized redistilled water. Reagent grade sodium thiosulfate pentahydrate (MCB reagent grade) was used without further purification. The silver ion was introduced as freshly precipitated and thoroughly dried silver chloride, prepared by mixing reagent grade silver nitrate (MCB reagent grade) and sodium chloride (Baker analyzed reagent). All solutions were prepared by weight. For each experimental run (not exceeding 3 hr) new solutions were prepared from dry components to minimize the effect of photodecomposition.

Results

The spectra of excess sound absorption, expressed as $\alpha_{\text{chem}}\lambda$ in nepers, vs. frequency show two apparent single relaxations within the range examined (Figure 1). The solid lines are the computer-simulated total absorption curve and composite single relaxation curves, respectively. Experimental data for all of the solutions studied are given in Table I.

In calculating the computer-simulated curves the data were fitted to the equation for total absorption in which it is assumed that the contributions from the single relaxations are additive

$$(\alpha_{\text{chem}}\lambda)_{\text{calcd}} = \frac{2(\alpha_{\text{chem}}\lambda)_1(f/f_1)}{1 + (f/f_1)^2} + \frac{2(\alpha_{\text{chem}}\lambda)_2(f/f_2)}{1 + (f/f_2)^2} \qquad (1)$$

In eq 1 f_1 and f_2 are the high and low relaxation frequencies, respectively, f is the experimental frequency, and $(\alpha_{\text{chem}}\lambda)_1$ and $(\alpha_{\text{chem}}\lambda)_2$ are the respective maximum amplitudes at the relaxation frequencies. Rather than solve eq 1 directly for the four parameters, the values were obtained from an iterative converging grid search routine. In this procedure, two 10 × 10 grids, whose initial wide limits spanned the approximate ranges of each relaxation frequency and each relaxation amplitude, were set up. Equation 1 was solved for all experimental frequencies using *all* combinations of points in the low-frequency grid for *each* point in the high-frequency grid. New narrower limits were set symmetrically around the points in each grid which gave the best correspondence between $(\alpha_{\text{chem}}\lambda)_{\text{calcd}}$ and $(\alpha_{\text{chem}}\lambda)_{\text{exptl}}$ in the previous cycle and the grid search was continued, by successive convergences, until the standard deviation σ^2 given by eq 2 was minimized. In

$$\sigma^2 = \sum_{i=1}^{n} \{[(\alpha_{\text{chem}}\lambda)_{i,\text{exptl}} - (\alpha_{\text{chem}}\lambda)_{i,\text{calcd}}]^2 W_i\} \qquad (2)$$

eq 2, n is the number of experimental points in the curve and W_i is a normalized weighting factor introduced to account for

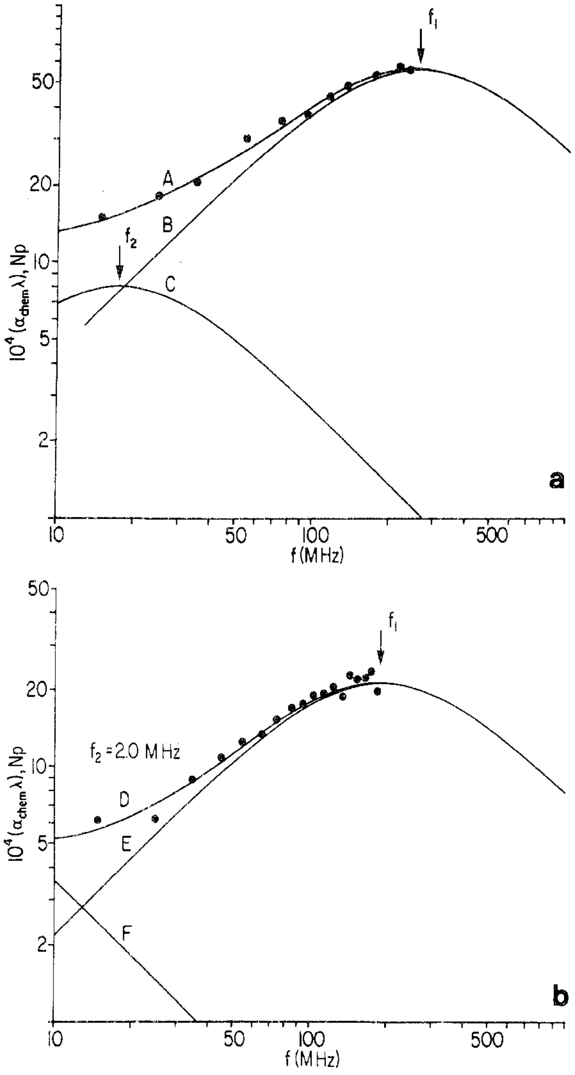

Figure 1. (a) Representative ultrasonic absorption curve A drawn through experimental points (black circles) obtained for an aqueous solution that is 0.50 *F* in sodium thiosulfate and 0.387 *F* in silver chloride. Curves B and C are theoretical and yield as their sum curve A. (b) Ultrasonic absorption curves similar to those in part (a) but for an aqueous solution that is 0.50 *F* in sodium thiosulfate and 0.20 *F* in silver chloride.

the relative precision in $(\alpha_{\text{chem}}\lambda)_{i,\text{exptl}}$. Convergence was usually accomplished in seven to eight passes. The resultant parameters and the goodness of fit expressed as the root-mean-square (rms) deviation are given in Table II. Precision in the data is inadequate to allow us to distinguish a possible third relaxation. Estimations of errors in the relaxation parameters are based on the analysis of Rassing and Lassen.[6] In the kinetic analysis the two relaxations have been assigned to two particular steps in the overall silver–thiosulfate complexation equilibria.

Silver thiosulfate complexation has been the subject of numerous equilibrium studies.[7] Evidence points to the existence of two predominant species, $AgS_2O_3^-$ and $Ag(S_2O_3)_2^{3-}$, formed according to the equations

$$Ag^+ + S_2O_3^{2-} \rightleftharpoons AgS_2O_3^- \tag{3}$$

$$AgS_2O_3^- + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} \tag{4}$$

with additional evidence for higher complexes[7] under particular experimental conditions, e.g., $Ag(S_2O_3)_3^{5-}$. Values for β_2, the overall stability constant, at 25° are on the order of 10^{13}. Since activity coefficients cancel in the expression for the thermodynamic β_2, the value is independent of the ionic strength of the medium, as shown by

$$\beta_2 = \frac{[AgL_2^{3-}]\gamma_3}{[Ag^+][L^{2-}]^2\gamma_1\gamma_2^2} \tag{5}$$

where $L^{2-} = S_2O_3^{2-}$, $\gamma_3 = \gamma_1^9$, and $\gamma_2 = \gamma_1^4$. Literature values for the stepwise formation constants,[8] which are dependent upon the ionic strength, are $K_1 = 6.6 \times 10^8$ and $K_2 = 4.4 \times 10^4$; cf. eq 6 and 7, where γ_1 is the activity coefficient of a

$$K_1 = \frac{[AgL^-]}{[Ag^+][L^{2-}]\gamma_1^4} \tag{6}$$

$$K_2 = \frac{[AgL_2^{3-}]\gamma_1^4}{[AgL^-][L^{2-}]} \tag{7}$$

univalent ion. By comparison,[7] estimates of K_3 are on the order of 5. AgL and AgL_2^{3-} are therefore the predominant species in solution in this study. By combining eq 5–7 with the equations for total analytical silver, *m*

$$m = [Ag^+] + [AgL^-] + [AgL_2^{3-}] \tag{8}$$

total analytical thiosulfate, *s*

$$s = [L^{2-}] + [AgL^-] + 2[AgL_2^{3-}] \tag{9}$$

and charge balance

$$[Na^+] + [Ag^+] = [Cl^-] + 2[L^{2-}] + [AgL^-] + 3[AgL_2^{3-}] \tag{10}$$

an equation, cubic in $[L^{2-}]$, can be derived and solved for $[L^{2-}]$, i.e.

$$[L_2^-]^3 + \frac{\gamma_1^4 + (2m - s)K_2}{K_2}[L^{2-}]^2 + \frac{K_2 + (m - s)\beta_2\gamma_1^4}{\beta_2 K_2}[L^{2-}] - \frac{s}{\beta_2} = 0 \tag{11}$$

Under the conditions of the experiment the s/β_2 term is insignificantly small compared to the remaining terms and eq 11 can be reduced to the quadratic form. An iterative procedure was used in the solution of eq 11, γ_1 being calculated from the Davies equation[9]

$$-\log \gamma_1 = 0.509\left\{\frac{\mu^{1/2}}{(1 + \mu^{1/2})} - 0.3\mu\right\} \tag{12}$$

in which μ, the ionic strength, is given by

$$\mu = {}^1/_2\{[Na^+] + [Ag^+] + [Cl^-] + [AgL^-] + 4[L^{2-}] + 9[AgL_2^{3-}]\} \tag{13}$$

The Davies equation is an approximation at the high ionic strength of the media used in this study but as such it offers the best theoretical estimation of γ_1. The results of the kinetic analysis are subject therefore to the theoretical limitations inherent to eq 12. Solution concentrations, equilibrium ion concentrations, and activity coefficients are given in Table III.

To assign the observed relaxations to specific steps in the complexation reaction, a mechanism must first be proposed for the entire process. Assuming a two-step mechanism for each ligand substitution according to the Diebler–Eigen scheme,[10] the complexation can be described as occurring in four steps, eq 14–17. Equations 14 and 16 describe the

$$Ag^+ + L^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ag^+(W)L^{2-} \tag{14}$$

$$Ag^+(W)L^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AgL^- \tag{15}$$

$$AgL^- + L^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} AgL^-(W)L^{2-} \tag{16}$$

$$AgL^-(W)L^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} AgL_2^{3-} \tag{17}$$

Table III. Results of Calculation of Equilibrium Concentrations Distribution and Concentration Terms for Kinetic Analysis[a]

$[L^{2-}]$, F	$[AgL_2^{3-}]$, F	$[AgL^-]$, F	$[Ag^+]$, F	γ_1^4	$\partial \ln\gamma_1^4/\partial \ln\beta$	θ	$\theta/(\theta + K_3^{-1})$
5.0×10^{-6}	0.113	0.274	$<10^{-7}$	0.533	−0.43	0.146	0.293
3.15×10^{-6}	0.091	0.218	$<10^{-7}$	0.416	−0.27	0.091	0.205
2.13×10^{-3}	0.248	2.13×10^{-3}	$<10^{-7}$	0.808	−1.08	1.6×10^{-3}	4.5×10^{-3}
0.10	0.200	4.54×10^{-3}	$<10^{-7}$	0.769	−0.86	0.011	0.031
0.20	0.150	1.70×10^{-5}	$<10^{-7}$	0.731	−0.65	0.052	0.129

[a] The results are presented for solution concentrations in the order they are presented in Table II.

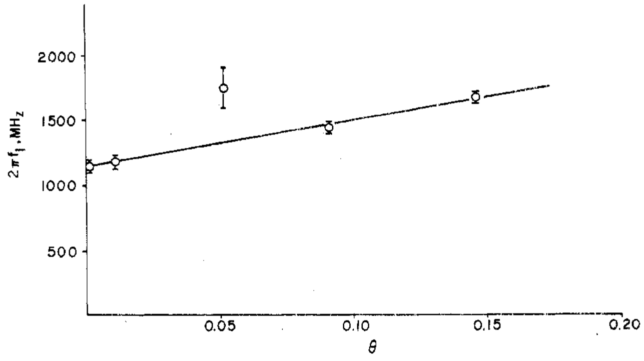

Figure 2. Plot of eq 20 of text with the slope yielding the specific rate $k_3 = 3.5 \times 10^9 \ M^{-1}$ sec^{-1} and the intercept $k_{-3} = 1.1 \times 10^9$ sec^{-1}. The solid diagonal is the linear least-squares fit of the experimental points. The vertical bars indicate estimated error.

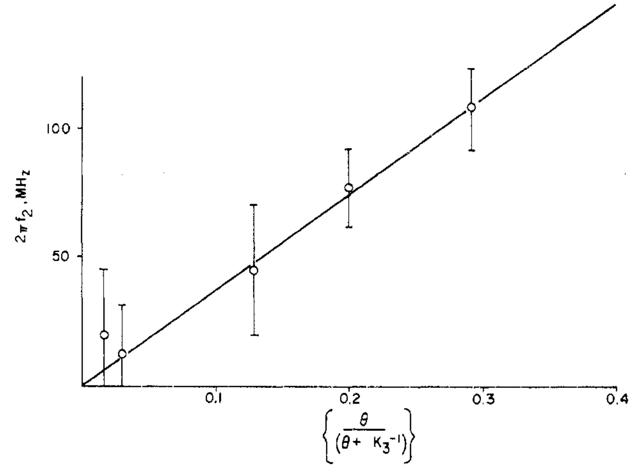

Figure 3. Plot of an equation equivalent to eq 21 of the text in which k_{-4} has been replaced by $k_4 K_4^{-1}$. The solid diagonal is a linear least-squares fit of the experimental data. The vertical bars indicate estimated error.

formation of two distinct solvent-shared or outer ion pairs, and eq 15 and 17 the successive substitutions into the first coordination sphere of Ag^+. Such a scheme would give rise to a continuous spectrum of relaxations characterized by at most four relaxation times. The problem is to assign the two observed relaxations to all or part of the overall mechanism, for which there are numerous alternatives. We believe that the most defensible interpretation is to assign the observed relaxations to steps 16 and 17 for the following reasons.

If the reactions 14 and 15 were perturbed by the progressive sound (pressure) wave, the rate equations for the reactions as they return to equilibrium would be given by[11]

$$2\pi f_1 = \phi k_1 + k_{-1} \tag{18}$$

$$2\pi f_2 = k_2\left\{\frac{\phi}{\phi + K_1^{-1}}\right\} + k_{-2} \tag{19}$$

where

$$\overline{K_1} = k_1/k_{-1}$$

and

$$\phi = \gamma_1^{-4}\left\{\overline{[Ag^+]} + \overline{[L^{2-}]}\left[1 + \left(\frac{\partial \ln \gamma_1^{-4}}{\partial \ln \beta}\right)\right]\right\}$$

β is the degree of association and the assumption is made that k_1, $k_{-1} >> k_2$, k_{-2}. From theory (see Discussion), $k_1 = 4.6 \times 10^{10} \ M^{-1}$ sec^{-1} and $k_{-1} = 0.9 \times 10^{10}$ sec^{-1}. Since from Table III it can be seen that $\phi \simeq [L^{2-}]$, the calculated $2\pi f_1$ varies from 1 to 2×10^{10} which places f_1 in the gigahertz range and out of the experimental range of the instrumentation. Furthermore, it has been pointed out (ref 11, p 961) that an equilibrium reaction with $K > 10^8$ is too "weak" to give any measurable contribution to sound absorption. The overall first association constant K_1 is 6.6×10^8. Either way the relaxation(s) associated with steps 14 and 15 are either too high in frequency or too low in amplitude to be observed. In addition the experimental data do not fit eq 18 and 19 in that whereas ϕ varies monotonically with total m at constant s, f_1 passes through a minimum value.

For either of the conditions described above for the relaxations associated with steps 14 and 15, little coupling with the relaxations for steps 16 and 17 would be expected. Equations analogous to (18) and (19) can therefore be written for the second association in which the AgL_2^{3-} complex is formed

$$2\pi f_1 = \theta k_3 + k_{-3} \tag{20}$$

$$2\pi f_2 = k_4\left\{\frac{\theta}{\theta + K_3^{-1}}\right\} + k_{-4} \tag{21}$$

where

$$K_3 = k_3/k_{-3}$$

and

$$\theta = \gamma_1^4\left\{\overline{[AgL^-]} + \overline{[L^{2-}]}\left[1 + \left(\frac{\partial \ln \gamma_1^4}{\partial \ln \beta}\right)\right]\right\}$$

The expansion of the partial derivative has been described previously.[12] Since $f_1 \simeq 20 f_2$, there is good reason to believe that there is little, if any, coupling between the two observed relaxations and that each relaxation frequency is characterized by only two rate constants; i.e., the assumption that k_3, $k_{-3} >> k_4$, k_{-4} appears to hold, and the approximate rate equations [(20) and (21)] are valid.

The rate constants for the second association step (Figures 2 and 3 obtained from the graphical solutions of eq 20 and 21) are $k_3 = 3.5 \times 10^9 \ M^{-1}$ sec^{-1}, $k_{-3} = 1.1 \times 10^9$ sec^{-1}; $k_4 = 3.7 \times 10^8$ sec^{-1}, $k_{-4} = 2.7 \times 10^4$ sec^{-1}. Error bars (in Figure 3) are greater on $2\pi f_2$ since the low-frequency relaxation is lower in amplitude and the maximum falls at the limit to or beyond the experimental frequency range. The solid lines are the linear least-squares fit through the experimental data. k_{-4} could not be obtained accurately from the almost zero intercept on the $2\pi f_2$ axis. Consequently, the least-squares line was drawn through the origin, and k_{-4} was calculated from the equilibrium constant K_4 and the slope k_4; i.e., $k_{-4} = k_4/K_4$. K_4 is related to K_2, the overall equilibrium constant for the second association, by the expression $K_2 = K_3(1 + K_4)$.

Discussion

The insensitivity of the first equilibrium in the overall process to perturbation by the propagating sound wave has made it impossible for us to measure the rate parameters for this step. One would assume that the rate of formation of the solvent-shared ion pair $Ag(W)L^-$ is diffusion controlled and a value for k_1 can be calculated from the Debye phenomenological equation[13]

$$k_1 = \frac{4\pi N Z_1 Z_2 e_0^2 (D_A + D_B)}{10^3 \epsilon k T \left[\exp\left(\frac{Z_1 Z_2 e_0^2}{\epsilon k T \mathring{a}}\right) - 1\right]} \qquad (22)$$

Using diffusion coefficients of 1.65×10^{-5} and 2.33×10^{-5} $cm^2\ sec^{-1}$ for Ag^+ and L^{2-}, respectively (calculated from limiting mobilities[14] of Ag^+ and L^{2-}), and a distance of closest approach parameter $\mathring{a} = 5 \times 10^{-8}$ cm, the value of k_1 calculated is 4.6×10^{10} M^{-1} sec^{-1}. There is, however, no analogous method to calculate k_2 the specific rate constant for what is presumably the rate-controlling step in the first substitution. By analogy k_3 can be calculated using eq 22 assuming diffusion control in the formation of the second solvent-shared ion pair $AgL(W)L^{3-}$. Since this step involves the diffusive approach of two anions, k_3 should be considerably less than k_1. Using a diffusion coefficient of 1.51×10^{-5} cm^2 sec^{-1} for AgL^-, equivalent to 65% of L^{2-} (cf. HSO_4^- vs. SO_4^{2-}), and $\mathring{a} = 5 \times 10^{-8}$ cm, a value of 2.6×10^9 M^{-1} sec^{-1} is obtained for k_3. The value is in very good agreement with the experimental value for $k_3 = 3.5 \times 10^9$ M^{-1} sec^{-1}. Furthermore, the value of $K_3 = k_3/k_{-3}$ of 3.2 is also in very good agreement with the equilibrium constant of 5 calculated from the Fuoss theoretical equation[15] using the same distance parameter.

Without a value for k_2 we are unable to comment upon the effect of the first substituted ligand on the relative rates of first and second substitutions into the first coordination sphere of Ag^+. The present value for k_3 can only be considered typical of the rate of second substitution, which, when compared to values for other ligands, may confirm either a dissociative or associative mechanism. If the detailed mechanism is associative, k_3 should be ligand dependent.[4] To our knowledge only one other ligand, *o*-phenanthroline, has been examined kinetically.[16] In this stopped-flow study the overall backward rate constant k_6, for the addition of the second *o*-phenanthroline ligand was measured. From this and the stability constant of the bis complex $K = 10^7$, k_f, the overall forward rate constant for second substitution, was calculated to be 3.0×10^9 M^{-1} sec^{-1}. From a steady-state kinetic analysis[15] and by using our nomenclature for rate constants, k_f can be shown to be related to k_4 by the expression $k_f = K_3 k_4$. By using our values for K_3 and k_4, k_f for the bis(thiosulfato) complex is found to be 1.0×10^9 M^{-1} sec^{-1} which is indicative of an associative mechanism. Substitution into Ag^+ is therefore analogous to that for the transition elements of square-planar geometry,[3] e.g., Pt^{2+}. Although a coordination number of 2 is most generally favored by Ag^+, there are reports of higher coordinations.[7,17] Accordingly, coordinated water need not be lost in forming the activated complex prior to the approach of the entering ligand which can be accommodated instead in one of the higher coordination sites with the subsequent loss of water and internal rearrangement to linear geometry in the complex.

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Registry No. Ag^+, 14701-21-4; $S_2O_3^{2-}$, 14383-50-7; $Ag(S_2O_3)_2^{3-}$, 35884-06-1.

References and Notes

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