

Kinetics and Mechanism of the Reaction of the Ammoniated Electron with Sodium Thiosulfate in Liquid Ammonia

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The reaction of sodium with sodium thiosulfate in liquid ammonia was found to be second order, first order with respect to both the sodium and sodium thiosulfate concentrations. The sodium ion concentration was found to have a dominant influence on the net reaction rate, and a mechanism involving ion-paired species is proposed. The stoichiometry and reaction products were also determined.

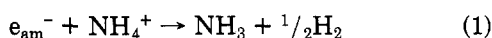
Introduction

Aside from the primary kinetic salt effect,^{1,2} rates of reactions between ions of the same charge can be markedly affected by inert ions of the opposite charge.² The latter specific ion effect is usually accounted for by formation of an ion pair which by shielding the electrostatic repulsion between the reactants facilitates the formation of the transition state. Recently, Hickel³ has demonstrated the above phenomenon by studying the effect of bivalent inert cations on the rate of the reaction of the solvated electron with the nitrate ion in ethanol. Similar behavior is expected for reactions of the ammoniated electron with negative ions. In the present work, we have studied the dissociative electron attachment reaction of the ammoniated electron with the thiosulfate ion in order to determine the effect of ion pair formation upon the rate. The primary kinetic salt effect acts in the same direction as ion pair formation,² but these effects on the rate constant can be distinguished by their relative magnitudes and by the addition of metal ion complexing agents.³

Experimental Section

Ammonia (Matheson, 99.99%) and sodium (United Mineral and Chemical Co.) were purified under vacuum conditions ($<10^{-6}$ torr) according to established procedures.^{4,5} Sodium thiosulfate (Fisher, certified reagent) was used as obtained without any further purification. Weighed samples of sodium thiosulfate were prepared in evacuated fragile ampules or break-seal tubes by methods described elsewhere.⁵ The reactions of sodium with sodium thiosulfate in liquid ammonia were carried out in a sealed borosilicate glass high-vacuum system. The progress of the reaction was monitored by utilizing conventional conductometric or spectrophotometric methods outlined in detail elsewhere.^{5,6}

Experiments were performed to establish the stoichiometry and products of the reaction of sodium with sodium thiosulfate in liquid ammonia. In these experiments an excess amount of sodium was used except in experiment NL-81, Table I. After the reaction of the thiosulfate with sodium was complete (readily determined by resistance measurements), an excess amount of ammonium chloride, via a break-seal tube, was added to the reaction mixture. The hydrogen evolved from reaction 1



was quantitatively collected as described elsewhere.⁴

The reaction between sodium thiosulfate and sodium in liquid ammonia was found to be consistent with eq 2.



The presence of sulfide ions as a product was confirmed

by the formation of hydrogen sulfide gas and zinc sulfide precipitate when an aqueous solution of the products was mixed with ammoniacal zinc chloride reagent. After the precipitation of the zinc sulfide, the mixture was filtered, and the filtrate was titrated by a standard iodometric method.⁷ This procedure allowed determination of the amount of sulfite ions present in the original product mixture. In other experiments, an aqueous solution of both products was titrated with the iodine solution so that the quantity of sulfide ions could be established by difference. Table I gives a summary of these experiments.

The results of experiments NL-62 and NL-74 (Table I) established that 2 mol of sodium was required to react completely with 1 mol of sodium thiosulfate to form 1 mol of sulfite ions (sulfide not determined). In experiments NL-81 and NL-84 (Table I) the sum of both the sulfide and sulfite ions was determined and was found to be in agreement with the quantities expected from eq 2.

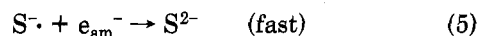
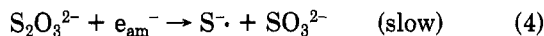
Results and Discussion

The reaction of the ammoniated electron with the thiosulfate ion was found to follow a second-order rate law, i.e., first-order with respect to each reactant:

$$-\frac{d(e_{am}^-)_T}{dt} = k_{obsd}(e_{am}^-)_T(Na_2S_2O_3)_T \quad (3)$$

where the subscript *T* denotes the total stoichiometric concentrations of sodium and sodium thiosulfate.

Figure 1 shows a representative plot of the relative sodium concentration (C/C_0) vs. time using the second-order rate expression, eq 3. The reaction products can be accounted for by the simple mechanism:



where the rate-determining step involves the cleavage of a S-S bond. Table II gives a summary of the kinetic data for the reaction of the ammoniated electron with the thiosulfate ion. While the observed second-order computer-generated plots gave excellent matches of theoretical to experimental data, it should be noted that the tabulated k_{obsd} values (Table II) are not constant. Moreover, the Brønsted-Bjerrum theory⁸ predicts an increase in rate with increasing ionic strength if the mechanism given by eq 4 and 5 is operative. However, the initial addition of (2,2,2)cryptand to the reaction mixture resulted in a marked effect on the reaction rate (experiment 3-84, Table II). This effect cannot be accounted for by the Brønsted-Bjerrum theory for the primary kinetic salt effect, and it strongly indicates a dependence of the sodium cation concentration on the net rate. Moreover, the ad-

TABLE I: Results of Product Analysis for the Reaction of Sodium with Sodium Thiosulfate in Liquid Ammonia at -45 °C

expt no.	initial Na, mmol	initial substrate, mmol	hydrogen collected, mmol	ratio of moles of Na to moles of substrate	product titrated	theoretical amount of product, mmol	actual amount collected, mmol
NL-62	0.942	0.261	0.205	2.04	sulfite	0.261	0.272
NL-74	2.20	0.966	0.171	1.92	sulfite	0.966	0.943
NL-81	1.28	0.709			sulfite and sulfide	1.28 ^a	1.27
NL-84	1.45	0.394			sulfite and sulfide	0.788	0.788

^a Based on the amount of sodium used.

TABLE II: Kinetic Data for the Reactions of Sodium with Sodium Thiosulfate in Liquid Ammonia

expt no.	10 ⁴ (sodium concn), M	$\left(\frac{[\text{Na}^+]}{K_8 + [\text{Na}^+]}\right)^2 \times 10^2$	10 ³ (Na ₂ S ₂ O ₃ concn), M	k _{obsd} , ^c M ⁻¹ s ⁻¹	temp, °C
2-3	7.60	6.89	1.05	1.70	-34
2-5	7.10	7.41	1.24	1.67	-34
2-27	0.89	4.62	1.26	1.47	-34
2-26	8.75	11.1	1.77	2.61	-34
2-29	32.5	19.0	1.84	5.01	-34
2-38	44.6	23.3	2.26	5.74	-34
2-92	16.5	15.2	2.35	3.02	-34
2-49	10.7	13.0	2.39	2.53	-34
3-84 ^a	6.03	~10 ⁻⁶	2.06	~10 ⁻²	-34
2-33	25.5	22.2	1.81	1.47	-45
2-34	3.46	12.3	1.86	0.73	-45
2-36	11.0	19.0	2.55	1.02	-45
2-37	8.5	16.9	2.30	1.02	-45
2-44	14.7	28.9	5.36	1.72	-45
3-90 ^b	4.59	60.5	2.98	4.40	-45
2-40	1.78	21.1	2.72	0.22	-65
2-41	16.4	27.6	2.72	0.25	-65
2-42	25.2	35.0	4.02	0.36	-65
2-43	9.96	20.6	1.77	0.20	-65

^a 5.614 × 10⁻⁴ mol of (2,2,2)cryptand added. ^b 3.98 × 10⁻² mol of NaCl added. ^c All the K_{obsd} values have a standard deviation of less than 5%.

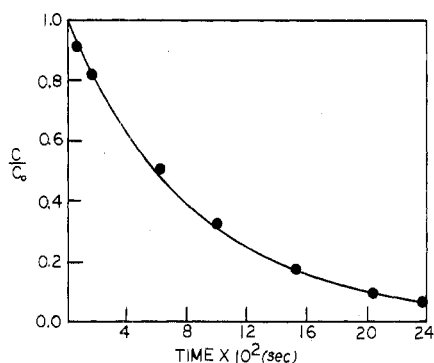
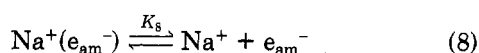
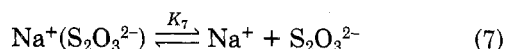
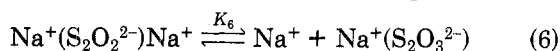


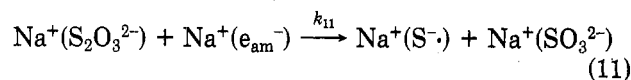
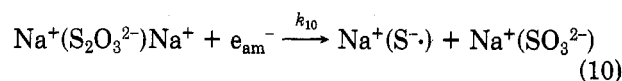
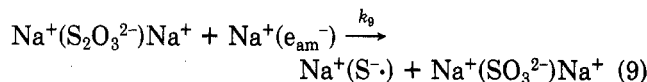
Figure 1. Representative C/C₀ vs. time plot for the reaction of sodium with sodium thiosulfate in liquid ammonia (expt 3-41).

dition of NaCl (Table II) resulted in a marked increase in the reaction rate. This increase is also larger than expected from considerations of the primary kinetic salt effect only. The above results, namely the experiments with added NaCl or (2,2,2)cryptand, strongly indicate that ion-paired species play a major role in determining the rate of the reaction of the ammoniated electron with the thiosulfate ion and that the mechanism given by eq 4 and 5 must be modified in order to account for the observed data.

Extensive ion-pairing would be expected in liquid ammonia because of its relatively low dielectric constant.⁹ The following ion-pairing equilibria are expected:



Therefore, the S-S bond cleavage step, reaction 4, can be represented by five other equations involving the various combinations of paired and unpaired thiosulfate species reacting with the paired or unpaired ammoniated electron; i.e., six possible reactions can be expected to take place simultaneously. A complete kinetic analysis of these reactions is not possible since the ion-pairing constants for eq 6 and 7 are not known. However, the ion-pairing dissociation constant for reaction 8 has been reported,¹⁰ and the reaction represented by eq 7 would not be expected to occur to any extent.¹¹ Therefore, the observed rate should result from the following three reactions:



The observed reaction rate can be taken as a linear combination of the rates for reactions 9, 10, and 11 such that:

$$-\frac{1}{2} \left(\frac{d(\text{e}_{\text{am}}^-)_T}{dt} \right) = k_{\text{obsd}}[\text{Na}]_T[\text{Na}_2\text{S}_2\text{O}_3]_T = R = k_9[\text{Na}^+(\text{e}_{\text{am}}^-)][\text{Na}^+(\text{S}_2\text{O}_3^{2-})\text{Na}^+] + k_{10}[\text{e}_{\text{am}}^-][\text{Na}^+(\text{S}_2\text{O}_3^{2-})\text{Na}^+] + k_{11}[\text{Na}^+(\text{e}_{\text{am}}^-)][\text{Na}^+(\text{S}_2\text{O}_3^{2-})] \quad (12)$$

With the aid of the appropriate material balance equations

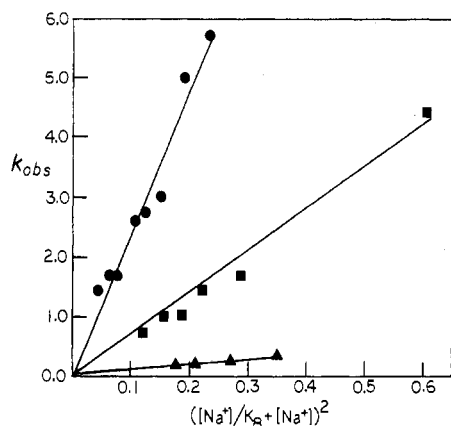


Figure 2. Plots of k_{obs} vs. $([\text{Na}^+]/K_8 + [\text{Na}^+])^2$ for the reaction of sodium with sodium thiosulfate in liquid ammonia. The circles, squares, and triangles represent data at -34 , -45 , and -65 °C, respectively.

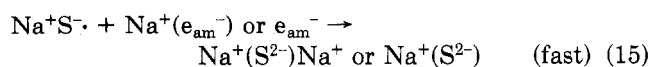
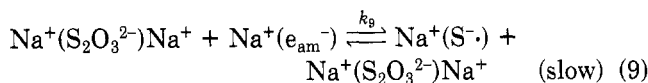
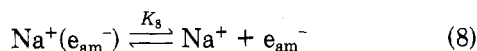
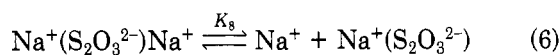
and assuming that $K_8 \approx K_6 = 1/K_A$, eq 12 can be written as:

$$R = \left(\frac{k_9 K_A^2 [\text{Na}^+]^2 + (k_{10} + k_{11}) K_A [\text{Na}^+]}{1 + 2K_A [\text{Na}^+] + K_A^2 [\text{Na}^+]^2} \right) \times [\text{Na}]_T [\text{Na}_2\text{S}_2\text{O}_3]_T \quad (13)$$

where $[\text{Na}^+]$ is the concentration of the free sodium cation and is essentially constant for any particular experiment. It should also be noted that we have obtained the empirical relationship reported by Olson and Simonson,¹² namely, eq 14, which is commonly used to analyze complex elec-

$$k_{\text{obsd}} = \left(\frac{k_9 K_A^2 [\text{Na}^+]^2 + (k_{10} + k_{11}) K_A [\text{Na}^+]}{1 + 2K_A [\text{Na}^+] + K_A^2 [\text{Na}^+]^2} \right) \quad (14)$$

trolytic reactions.¹³ In eq 14, k_{obsd} and $[\text{Na}^+]$ can be considered to be variables while k_9 , k_{10} , and k_{11} are the adjustable parameters. When a general least-squares curve-fitting program¹⁴ was used to find the parameters (k_{10} and k_{11}) with minimum standard deviation from data given in Table II, it was concluded that k_{10} and k_{11} are close to zero and hence reactions 10 and 11 do not contribute to any measurable extent to the net rate. Moreover, this indicates that only the reactions involving fully paired species contribute significantly to the observed ion-paired rate. The reaction mechanism is therefore best described by the following scheme:



The rate law based on the above reaction mechanism is then

$$-\frac{d(\text{e}_{\text{am}}^-)}{dt} = 2k_9 \left(\frac{[\text{Na}^+]}{K_8 + [\text{Na}^+]} \right)^2 [\text{Na}]_T [\text{Na}_2\text{S}_2\text{O}_3]_T \quad (16)$$

The mechanism is consistent with the observed second-order kinetics and can account for the dependence of the rate constant on the sodium cation concentration. Figure 2 gives plots of k_{obsd} vs. $([\text{Na}^+]/K_8 + [\text{Na}^+])^2$, at three temperatures, and the obtained linear relationship

TABLE III: Summary of the Kinetic Constants for the Reaction of Sodium with Sodium Thiosulfate in Liquid Ammonia^a

k_9 , $\text{M}^{-1} \text{s}^{-1}$	temp, °C
12.1 ± 0.51	-34
3.86 ± 0.42	-45
0.52 ± 0.10	-65

^a $E_a = 41.9 \pm 2.1 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 40.0 \pm 2.1 \text{ kJ mol}^{-1}$, calculated at -34 °C; $\Delta S^\ddagger = -55.1 \pm 2.3 \text{ J mol}^{-1} \text{ deg}^{-1}$, calculated at -34 °C.

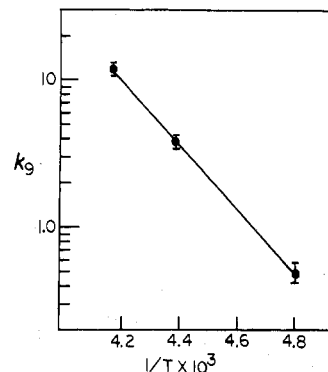


Figure 3. Semilog plot of k_9 vs. $1/T$ for the reaction of sodium with sodium thiosulfate in liquid ammonia.

strongly supports the proposed mechanism. Also, it should be noted that the straight lines shown in Figure 2 extrapolate to the origin which is in agreement with K_{obsd} approaching zero as the free sodium ion concentration approaches zero. This fact is also consistent with the experiment involving (2,2,2)cryptand.

The constant, k_9 , can readily be evaluated from the slopes of the straight lines given in Figure 2. A semilog plot of k_9 vs. $1/T$ is shown in Figure 3. Table III gives a summary of the calculated kinetic parameters obtained in this study. The negative entropy of activation can be attributed to the collapse of the cavity of the ammoniated electrons¹⁵ and appears again to demonstrate a specific characteristic of reactions involving ammoniated electrons.

The kinetic data of this present study strongly support the contention that the rate-determining reaction is one between ion-paired species. The interaction of the ion-paired species would tend to minimize electron-electron repulsion which is probably the dominant factor in influencing the rates of dissociative electron attachment reactions such as those given by eq 4 or 9. Finally, we should point out that we exposed solutions of sodium sulfite and sodium sulfate to sodium-ammonia solutions and observed no measurable reaction. This confirmed that the sulfate produced from the thiosulfate reaction is inert to further reaction with the ammoniated electron.

References and Notes

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