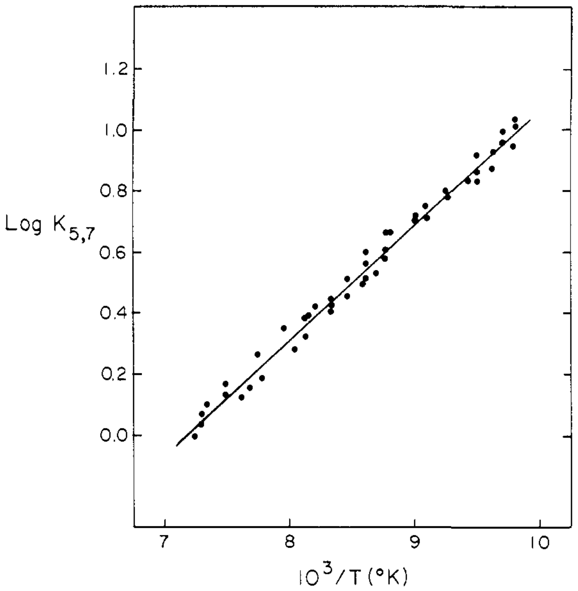

Figure 3. van't Hoff plot for $H_5^+ + H_2 \rightleftarrows H_7^+$. Standard state = 1 atm. $P_{H_2}$ = 4.3 Torr.

−13.1 ± 0.9 eu. The values extrapolated to zero repeller voltage are given in Table II. Nonlinear behavior is not observed here since at the lowest temperature attainable (−171°) the product to reactant ion ratio has just reached 5%.

## Discussion

Although it is encouraging that there is good agreement in the absolute magnitude of $K_{3,5}$ between the present results and those of Arifov, *et al.*, their $\Delta H°$ and $\Delta S°$ values do not agree well with ours. Although impure hydrogen was employed by Arifov, *et al.*, judging by the presence of copious quantities of $N_2H^+$ and $H_3O^+$ plus higher hydrates (see table in ref 8), the important fact to be observed is that their 3,5-equilibrium constant has been measured over a very narrow temperature range. Furthermore, the temperature range over which their data were obtained corresponds to the nonlinear region of our data. Their $H_5^+$ to $H_3^+$ intensity ratio was 1.1 at 40 Torr and room temperature.[8] Our experience has been that nonlinear behavior sets in when the product to reactant ratio is greater than approximately 0.1. Hence we suspect the data of Arifov, *et al.*, are not at equilibrium, and that their measurements could have profitably been extended to higher temperatures.

The association ion $H_7^+$ is indeed weakly bound. This is experimentally manifested in the fact that it does not appear in the spectrum at temperatures above about −135°. The entropy change for the 5,7 reaction is somewhat more positive than that for the 3,5-reaction, and is due probably to the lower binding energy of $H_7^+$ and its weaker, low frequency vibrational modes relative to $H_5^+$.

**Acknowledgment.** This work was supported in part by the National Science Foundation.

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# Kinetics of Disproportionation of Radical Anions of Tetraphenylethylene Induced by Flash Photolysis. Effect of Ionic Aggregations on the Rate of Disproportionation

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**Abstract:** Flash photolysis of an equilibrium mixture of tetraphenylethylene (T) and of sodium salts of its radical anion ($T\cdot^-$) and dianion ($T^{2-}$) leads to ejection of electrons from $T^{2-}$ followed by their capture by T. Thus, the equilibrium is upset, the concentration of $T\cdot^-$ increases and that of T and $T^{2-}$ decreases. In the dark period following the flash the system returns to equilibrium. The kinetics of this relaxation was investigated. It was found that the equilibrium is reestablished by reaction 2, ($T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+$) $k_2 = 10 \times 10^6\ M^{-1}\ sec^{-1}$ and $k_{-2} = 3 \times 10^6\ M^{-1}\ sec^{-1}$. Rates of reactions 1 ($2T\cdot^-,Na^+ \rightleftarrows T + T^{2-},2Na^+$) and 3 ($2T^- \rightleftarrows T + T^{2-}$) are too slow to contribute significantly to the rate of the observed process. The equilibria 1 and 3 are reestablished through rapid dissociation–associations of ionic species, *e.g.*, $T\cdot^-,Na^+ \rightleftarrows T\cdot^- + Na^+$ and $T^{2-},2Na^+ \rightleftarrows T^{2-},Na^+ + Na^+$, which accompany reaction 2.

Disproportionation of radical anions of tetraphenylethylene (T) was studied by several research groups[1,2] who focussed their interest on the equilibrium established in the system $2T\cdot^- \rightleftarrows T^{2-} + T$ ($T\cdot^-$ and $T^{2-}$ denote the radical anion and the dianion of T, respectively). In most solvents used in such studies the anions and dianions are paired, at least partially, with the cations and therefore it is necessary to differentiate among the individual equilibria, *e.g.*,

$$2T\cdot^-,Na^+ \rightleftarrows T^{2-},2Na^+ + T \qquad K_1$$

$$T\cdot^-,Na^+ + T^-\cdot \rightleftarrows T^{2-},Na^+ + T \qquad K_2$$

$$2T\cdot^- \rightleftarrows T^{2-} + T \qquad K_3$$

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(1) (a) A. G. Evans and B. J. Tabner; *J. Chem. Soc.*, 4613 (1963); (b) J. F. Garst and R. S. Cole; *J. Amer. Chem. Soc.*, **84**, 4352 (1962); (c) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, **86**, 2257 (1964); (d) J. F. Garst and E. R. Zabolotny, *ibid.*, **87**, 495 (1965).

(2) (a) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965); (b) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

**Table I.** Experimental Conditions

| No. | $[T\cdot^-_{\text{total}}]$ $\times 10^6\ M$ | $[T^{2-}_{\text{total}}]$ $\times 10^6\ M$ | $[T]$ $\times 10^6\ M$ | $[Na^+]$ $\times 10^6\ M$ | $[Na^+, BPh_4^-]$ $\times 10^6\ M$ |
|---|---|---|---|---|---|
| 1. Initial | 0.87 | 2.6 | 11.6 | 137 | |
| Equilibrium | 0.49 | 2.8 | 11.4 | 137 | 350 |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 0.73$ | | | |
| 2. Initial | 0.46 | 2.75 | 1.01 | 140 | |
| Equilibrium | 0.15 | 2.9 | 1.16 | 140 | 356 |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 0.71$ | | | |
| 3. Initial | 1.44 | 2.7 | 9.5 | 36 | |
| Equilibrium | 1.00 | 2.9 | 9.7 | 36 | 50 |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 2.8$ | | | |
| 4. Initial | 0.65 | 1.75 | 0.86 | 24.7 | |
| Equilibrium | 0.35 | 1.90 | 1.01 | 24.2 | 30.4 |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 4.1$ | | | |
| 5. Initial | 0.295 | 0.44 | 0.10 | 8.2 | |
| Equilibrium | 0.181 | 0.50 | 0.16 | 8.1 | 8.6 |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 12.3$ | | | |
| 6. Initial | 3.16 | 2.62 | 1.17 | 3.57 | |
| Equilibrium | 2.77 | 2.82 | 1.37 | 3.28 | None |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 29$ | | | |
| 7. Initial | 3.51 | 2.77 | 1.00 | 3.83 | |
| Equilibrium | 2.46 | 2.82 | 1.37 | 3.28 | None |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 28$ | | | |
| 8. Initial | 2.23 | 0.92 | 0.55 | 2.42 | |
| Equilibrium | 1.85 | 1.11 | 0.74 | 2.12 | None |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 44$ | | | |
| 9. Initial | 1.64 | 0.59 | 0.29 | 1.81 | |
| Equilibrium | 1.49 | 0.66 | 0.36 | 1.68 | None |
| | | $[T\cdot^-]/[T\cdot^-,Na^+] = 57$ | | | |

This point was not appreciated in the early investigations and consequently the reported results provided the values of the apparent equilibrium constant

$$K_{\text{ap}} = [T^{2-}_{\text{total}}][T]/[T\cdot^-_{\text{total}}]^2$$

where $[T^{2-}_{\text{total}}]$ and $[T\cdot^-_{\text{total}}]$ denote the *total* concentrations of the dianions or radical anions irrespective of their form of aggregation. The individual equilibrium constants were determined in later investigations,[1d,2] *e.g.*, $K_1$ and $K_2$ were determined for the sodium salts in tetrahydrofuran[2a] and $K_3$ for the free ions dissolved in hexamethylphosphoric triamide.[2b]

Recently we investigated the kinetics of these disproportionations by adopting the following approach. The equilibrium mixture of T and of the salts of $T\cdot^-$ and $T^{2-}$ is flash photolyzed. The light photoejects electrons from $T^{2-}$ and these are rapidly captured by T which then is reduced to $T\cdot^-$. Thus, the equilibrium is upset, the concentration of radical anions is increased while the concentrations of the parent hydrocarbon and of the dianions are reduced accordingly. In the dark period following the flash the system returns to its state of equilibrium and this relaxation is followed spectrophotometrically by monitoring the absorbences of $T\cdot^-$ or $T^{2-}$.

The absorption bands of $T\cdot^-$ and $T^{2-}$ are relatively broad and therefore it is plausible to assume that the extinction coefficients of these species at their respective maxima are virtually unaffected by their coupling with counterions. Moreover, examination of the conditions maintained in our experiments (see Table I) shows that even if the pairing somewhat affects the relevant extinction coefficients, the kinetic results obtained in each individual run would be insignificantly modified.

In presenting this work we shall examine first the mathematical aspects of the kinetics of the investigated relaxation and deduce the equations permitting the calculation of the pertinent rate constants. Thereafter, we shall describe the experimental details and the relevant results, and finally discuss their significance.

## Kinetics of the Dark Reaction

The following three reactions

$$2T\cdot^-,Na^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} T^{2-},2Na^+ + T \qquad K_1 = 400 \quad (1)$$

$$T\cdot^-,Na^+ + T\cdot^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} T^{2-},Na^+ + T \qquad K_2 = 3.3 \quad (2)$$

$$2T\cdot^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} T^{2-} + T \qquad K_3 < 10^{-8} \quad (3)$$

in conjunction with the rapidly established ionic equilibria

$$T\cdot^-,Na^+ \rightleftarrows T\cdot^- + Na^+ \qquad K_{D1} = 10.0 \times 10^{-5}\ M \quad (4)$$

$$T^{2-},2Na^+ \rightleftarrows T^{2-},Na^+ + Na^+ \qquad K_{D2} = 8.3 \times 10^{-7}\ M \quad (5)$$

$$T^{2-},Na^+ \rightleftarrows T^{2-} + Na^+ \qquad K_{D3} < 10^{-12}\ M \quad (6)$$

govern the return of the investigated system to its state of equilibrium. The values for $K_1$, $K_2$, $K_{D1}$, and $K_{D2}$ are taken from ref 2a. They were determined at ambient temperature for the reaction proceeding in tetrahydrofuran (THF). The value of $K_{D3}$ was estimated; the approach based on simple electrostatics demonstrates that the free energy of dissociation (eq 6) should be at least twice as large as that of dissociation (eq 5). Hence, $K_{D3}$ should be smaller than $10^{-12}\ M$. The constants $K_1$, $K_2$, $K_{D1}$ and $K_{D2}$, and $K_2$, $K_3$, $K_{D1}$, and $K_{D3}$ are related through the equations

$$K_1/K_2 = K_{D1}/K_{D2} \text{ and } K_2/K_3 = K_{D1}/K_{D3}$$

respectively. Therefore, $K_3$ should be smaller than $10^{-8}$ provided $K_{D3} < 10^{-12}$ $M$. The low magnitude of $K_3$ is expected since even in hexamethylphosphoric triamide (HMPA), a solvent of a substantially higher dielectric constant and solvating power than THF, the direct determination [2b] of $K_3$ led to a value of $2 \times 10^{-4}$ only.

At the equilibrium, the relation between the total concentration of radical ions, $T\cdot^{-}_{total} = T\cdot^{-},Na^{+} + T\cdot^{-}$, and the total concentration of dianions,[3] $T^{2-}_{total} = T^{2-},2Na^{+} + T^{2-},Na^{+}$, is given[2a] by the equation

$$[T^{2-}_{total}]_e[T]_e/[T\cdot^{-}_{total}]_e^2 = K_1(1 + K_{D2}/[Na^+]_e)/(1 + K_{D1}/[Na^+]_e)^2$$

the subscript "e" denoting the equilibrium concentration of the reagents.

Flash photolysis ejects electrons from the dianions and these electrons are rapidly captured by the parent hydrocarbon, T. Hence, at the end of the flash the concentration of radical ions increases by $x_0$ while the concentrations of the dianions and of the parent hydrocarbon decreases by $^1/_2x_0$. Thus, the initial concentrations of the reagents at the beginning of the dark reaction are $[T\cdot^{-}_{total}]_e + x_0$, $[T^{2-}_{total}]_e - {}^1/_2x_0$ and $[T]_e - {}^1/_2x_0$, respectively.

The return to the state of equilibrium is relatively slow; it requires a few seconds under conditions of our experiments. Hence, during the course of the observed process the ionic equilibria (4–6) are maintained at each momentary concentration of the reagents. The rate is given by

$$-dx/dt = \{k_1[T\cdot^{-},Na^+]^2 - k_{-1}[T^{2-},2Na^+][T]\} + \{k_2[T\cdot^{-},Na^+][T\cdot^{-}] - k_{-2}[T^{2-},Na^+][T]\} + \{k_3[T\cdot^{-}]^2 - k_{-3}[T^{2-}][T]\}$$

It seems that the last bracket term in the above sum may be neglected. Since $K_3 < 10^{-8}$, the rate constant $k_3$ must be smaller than $10^3$ $M^{-1}$ sec$^{-1}$ even if the reverse reaction is diffusion controlled, *i.e.*, $k_{-3} \sim 10^{10}$–$10^{11}$ $M^{-1}$ sec$^{-1}$. The low value of $k_3$ is not surprising because the repulsion between the two negatively charged $T\cdot^{-}$ ions considerably reduces the rate of their interaction. The term $k_{-3}[T^{2-}][T]$ also is expected to be negligible because the concentration of the free $T^{2-}$ ions is exceedingly low. Hence

$$-dx/dt = k_{-1}\{K_1(1 + K_{D1}/[Na^+])^{-2}[T\cdot^{-}_{total}]^2 - -(1 + K_{D2}/[Na^+])^{-1}[T^{2-}_{total}][T]\} + k_{-2}\{K_2(K_{D1}/[Na^+])(1 + K_{D1}/[Na^+])^{-2}[T\cdot^{-}_{total}]^2 - (K_{D2}/[Na^+])(1 + K_{D2}/[Na^+])^{-1}[T^{2-}_{total}][T]\}$$

Further simplification is possible by substituting $[T\cdot^{-}_{total}]_e + x$, $[T^{2-}_{total}]_e - {}^1/_2x$ and $[T]_e - {}^1/_2x$ for the concentrations of the respective reagents and using the relation $K_1/K_2 = K_{D1}/K_{D2}$. Thus

$$-dx/dt = (k_{-1} + k_{-2}K_{D2}/[Na^+])(ax + bx^2) = (k_1 + k_2K_{D1}/[Na^+])K_1^{-1}(ax + bx^2)$$

where

$$a = 2K_1(1 + K_{D1}/[Na^+])^{-2}[T\cdot^{-}_{total}]_e + {}^1/_2(1 + K_{D2}/[Na^+])^{-1}([T^{2-}_{total}]_e + [T]_e)$$

and

$$b = K_1(1 + K_{D1}/[Na^+])^{-2} - {}^1/_4(1 + K_{D2}/[Na^+])^{-1}$$

Integration leads then to the result

$$a^{-1} \ln \{(a + bx)/x\} = (k_{-1} + k_{-2}K_{D2}/[Na^+])t$$

provided the concentration of $Na^+$ ions remains virtually constant during the reaction. It will be shown subsequently that under conditions chosen for our experiments this indeed is the case.

It follows from the above treatment that a plot of $a^{-1} \ln \{(a + bx)/x\}$ *vs.* time should be linear, its slope, $k_{obsd}$, giving $k_{-1} + k_{-2}K_{D2}/[Na^+] = (k_1 + k_2K_{D1}/[Na^+])/K_1$. Hence, on plotting $k_{obsd}$ *vs.* $K_{D2}/[Na^+]$ one should obtain a straight line with a slope equal to $k_{-2}$ and an intercept giving $k_{-1}$.

It should be stressed that the values of $k_{obsd}$ do not determine the relaxation time of the investigated process. The reciprocal of the relaxation time for low $x$ values is related to the product $ak_{obsd}$ and the latter reaches a constant value for sufficiently low concentrations of sodium ions, because an increase of $k_{obsd}$ is counterbalanced by a decrease of $a$.

## Experimental Section

Stock solutions of the salts of $T\cdot^{-}$ and $T^{2-}$ in tetrahydrofuran were prepared on a high vacuum line by controlled reduction of tetraphenylethylene with metallic sodium. The concentration of the reduced species in such solutions was about $10^{-3}$ $M$ and whenever it was necessary to increase the concentration of $Na^+$ ions a desired amount of sodium tetraphenylboride was added.

A stock solution was introduced through a breakseal into the storage bulb of an evacuated and decontaminated apparatus used in the photolysis. A cylindrical, 20-cm long quartz cell with optically flat windows was linked to the storage bulb of this apparatus. Its detailed description as well as the description of the procedure used in its decontamination and filling with the solution to be photolyzed are given elsewhere.[4] Suffice to say that the solvent was distilled from the storage bulb into the cell and thereafter a drop or two of the residual solution were added to the cell by tilting the unit. Thus, a highly dilute solution, about $10^{-6}$ $M$, was obtained without introducing any impurities in such a preparation. Moreover, by returning the contents of the cell into the storage bulb and then by repeating the previous procedure, a fresh dilute solution could be prepared virtually free of any decomposition products, even if such were produced by the previous flash photolysis.

The concentrations of the reagents in the individual experiments are listed in Table I. Their values were obtained spectrophotometrically by investigating the spectrum of the dilute solution before and after a flash. Visible light ($\lambda$ >420 nm) was used for the photolysis, radiation of shorter wavelength being absorbed by suitable filters. The storage bulb and the connecting tubes were protected from any exposure to the flash light by wrapping them with aluminum foil.

Progress of the dark reaction was determined by monitoring the absorbance of the light of a xenon lamp placed in front of the optical cell. A Zeiss monochromator and a photomultiplier linked to a scope permitted the recording of the absorbence at a particular wavelength as a function of time. The absorbence was measured at 480 nm, $\lambda_{max}$ of $T^{2-}$, or at 700 nm where $T\cdot^{-}$ absorbs. Typical photographs of the oscilloscope output are shown in Figure 1. The kinetic results were found to be independent of the wavelength chosen to monitor the reaction confirming, therefore, the stoichiometry of the reaction.

## Results

The spectra of the sodium salts of $T\cdot^{-}$ and $T^{2-}$ were reexamined. The pertinent extinction coefficients were redetermined and, as indicated by the results given below

| $\lambda$, nm | 370 | 480 | 660 |
|---|---|---|---|
| $10^{-4} \times \epsilon(T\cdot^{-})$ | 2.0 (max) | 0.8 | 1.13 (max) |
| $10^{-4} \times \epsilon(T^{2-})$ | 1.6 | 3.7 (max) | 0.13 |

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[3] The concentration of $T^{2-}$ is extremely low, and hence this species insignificantly contributes to $T^{2-}_{total}$.

[4] G. Rämme, M. Fisher, S. Claesson, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, 327, 467 (1972).

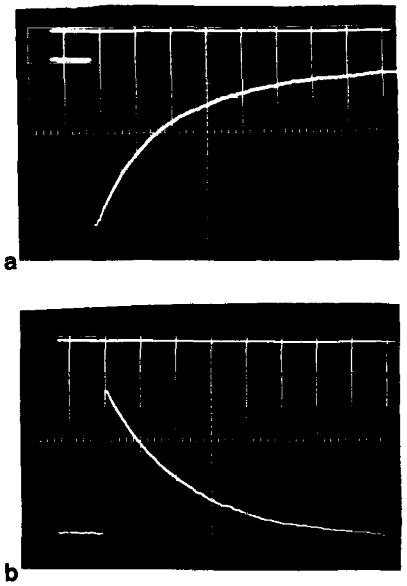

Figure 1. Oscilloscope traces obtained by monitoring light absorption during the disproportionation of tetraphenylethylene radical ions: (a) appearance of $T^{2-}$ after bleaching (λ 480 nm), time scale 0.5 sec/div; (b) disappearance of $T\cdot^-$ after the flash (λ 700 nm), time scale 0.5 sec/div.

they differ only slightly from those reported in the literature.[1d,2a]

Examination of the data collected in Table I shows that in each kinetic experiment the concentration of the sodium ions remained virtually constant during the course of the reaction. Therefore, the integration leading to the relation $a^{-1}$ ln $\{(a + bx)/x\} = (k_{-1} + k_{-2}K_{D2}/[Na^+])t$ is justified. Typical plots of ln $\{(a + bx)/x\}$ *vs.* time are shown in Figure 2, and its inspection demonstrates that the expected linear relations are maintained even up to 90% of the reaction. Their slopes permit us to calculate the values of $k_{obsd} = k_{-1} + k_{-2}\cdot K_{D2}/[Na^+]$ listed in Table II for various concentrations of $Na^+$ ions. The plot of $k_{obsd}$ *vs.* $K_{D2}/[Na^+]$ is shown in Figure 3. Its intercept is indistinguished from zero, indicating that $k_{-1} < 4 \times 10^4$ $M^{-1}$ sec$^{-1}$, and the slope gives $k_{-2} = 3 \times 10^6$ $M^{-1}$ sec$^{-1}$. Hence, $k_1 < 8 \times 10^6$ $M^{-1}$ sec$^{-1}$ and $k_2 = 10 \times 10^6$ $M^{-1}$ sec$^{-1}$. The experimental points in Figure 3 do not show upward deviations even for the lowest accessible concentrations of $Na^+$ ions (~1.6 × $10^{-6}$ $M$). This implies that $k_3$ is indeed very small, justifying the estimate given in the earlier part of this paper, *i.e.*, $k_3 < 10^3$ $M^{-1}$ sec$^{-1}$.

**Table II.** Kinetic Data for the Disproportionation of $T\cdot^-$ Radical Ions in THF at 25° ($Na^+$, counterions)

| No. | $10^3$ $K_{D2}/[Na^+]$ | $10^{-4}k_{obsd} = (k_{-1} + k_{-2}K_{D2}/[Na^+]) \times 10^{-4}$ $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 1 | 6.0 | 2.6 |
| 2 | 5.9 | 4.2 |
| 3 | 22.8 | 3.9 |
| 4 | 34 | 8.8 |
| 5 | 102 | 30.7 |
| 6 | 242 | 69.3 |
| 7 | 233 | 60.7 |
| 8 | 365 | 107 |
| 9 | 475 | 142 |

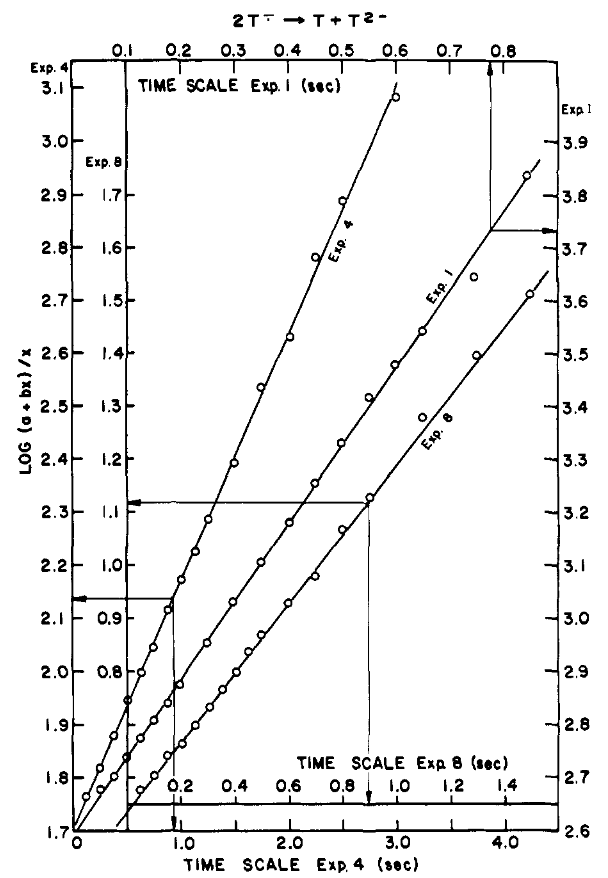

Figure 2. Plots of log $\{(a + bx)/x\}$ *vs.* time. The respective scales are marked by the arrows.

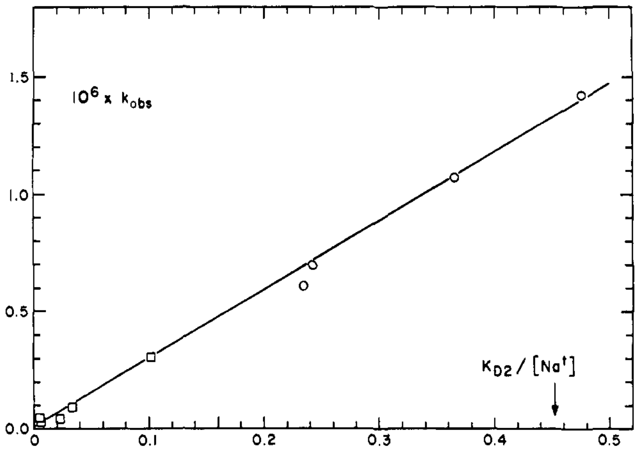

Figure 3. Plot of $k_{obsd}$ *vs.* $K_{D2}/[Na^+]$.

## Conclusions

The studies reported in this paper show that disproportionation 2, $T\cdot^- + T\cdot^-,Na^+ \rightarrow T + T^{2-},Na^+$, is faster than disproportionation 1, $2T\cdot^-,Na^+ \rightarrow T + T^{2-},2Na^+$, and also much faster than disproportionation 3, $2T^- \rightleftarrows T + T^{2-}$. These findings can be easily rationalized. In disproportionation 2 the attraction between the charged ion and the dipolar $Na^+,T\cdot^-$ ion pair stabilizes the transition state of the electron transfer and, most probably, only the electron, and not the counterion, has to be transferred in the process if the transition state $T\cdot^- \cdots Na^+,T\cdot^-$ is not symmetric in respect to both $T\cdot^-$'s. Both factors facilitate then the reaction. Although a feasible attraction between two dipoles may stabilize the transition state of reaction 1, such a process requires a transfer of Na$^+$ with the electron and this substantially slows down the reaction,[4,5] particularly if both Na$^+$ ions have to be dissolvated in the transition state. Such a desolvation, which probably also takes place in disproportionation 2, involves only one Na$^+$ ion. Finally, reaction 3 is hindered by the repulsion of two negatively charged ions; its rate seems to be by four or five powers of ten slower than the rate of 2. A recent illustration of the importance of the repulsion in electron transfer reactions was provided by Abley and Halpern[6] who found the reaction $BPh_4^- + (IrCl_2)^{2-} \rightarrow BPh_4\cdot + (IrCl_6)^{3-}$ to be substantially slower than the reaction $BPh_4. + (IrCl_6)^{2-} \rightarrow BPh_4^+ + (IrCl_6)^{3-}$, in spite of the fact that the ionization potential of $BPh_4^-$ is much lower than that of the $BPh_4\cdot$ radical.

The reverse reactions (1–3) are exothermic and could be expected to be very fast. Indeed, it is believed that the reverse of reaction 3 is diffusion controlled ($k_{-3} \sim 10^{10}$–$10^{11}$ $M^{-1}$ sec$^{-1}$). However, the reverse reactions 1 and 2 are relatively slow, $k_{-1} < 4 \times 10^4$ $M^{-1}$ sec$^{-1}$ and $k_{-2} = 3 \times 10^6$ $M^{-1}$ sec$^{-1}$. It is probable that the change of the geometry of the donor[2a] ($T^{2-}$,Na$^+$ or $T^{2-}$,2Na$^+$) occurring on its oxidation to the radical anion accounts for the relatively low value of $k_{-2}$ and a further decrease in the rate is expected for the reverse reaction 1 in which the tightly bounded Na$^+$ ion has to be transferred with the electron.

Finally we wish to report an interesting observation. Typical flash photolysis of $T^{2-}$ in THF led to 20% bleaching of its absorbence. Under the same conditions the bleaching was not observed when dioxane was substituted for THF as a solvent. A similar effect was noted previously in the flash photolysis of sodium pyrenide.[3] Its flash photolysis led to 70–80% of bleaching when THF was used as a solvent, but under the same conditions only 5% of bleaching was observed when the reaction was performed in tetrahydropyran. Sodium pyrenide forms loose pairs in THF but tight pairs in tetrahydropyran, and this difference in the structure was proposed as an explanation of the above phenomenon.[3] Apparently a similar situation is encountered in the present case. The $T^{2-}$ salt has different structure in THF and in dioxane and probably the aggregation is tighter in the latter solvent.

**Acknowledgment.** The financial support of this study by the Swedish National Science Research Council and the National Science Foundation (U. S. A.) is gratefully acknowledged.

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(5) *E.g.*, N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem Soc.*, **90**, 3611 (1968); earlier references are given in this paper.

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# Binding of Hydrogen Donors by Peptide Groups of Lactams. Identity of the Interaction Sites

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*Contribution from the Department of Chemistry, Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121.* *Received May 24, 1972*

**Abstract:** Binding of hydrogen donors [$CH_2Cl_2$, $CH_3OH$, $CHCl_3$, water, and $CH_3COOH$ (glacial)] by poly(1-vinyl-2-pyrrolidinone) and by its monomeric analog 1-ethyl-2-pyrrolidinone was studied by infrared, spin-echo, and viscosity measurements. Water is the most strongly bound, $CH_2Cl_2$ the weakest. Binding takes place not only at the carbonyl bond of the lactams but also involves the C–N bond which results in an appreciable decrease in the conjugation of the peptide linkage and loss of partial double bond character of the C–N bond. The data on 1-ethyl-2-pyrrolidinone show that a relatively large number of lactam-water species of different composition are formed rather than a well-defined complex as is generally assumed. Hydrogen donor binding by the polymer is weaker than by the monomer, possibly because of the interference of binding sites. The apparent failure of viscosity data to accurately predict the stoichiometry of solution complexes is pointed out.

The interaction between water and peptide groups has significant influence on such phenomena as the conformational behavior of polypeptides and other biological macromolecules,[1–6] the ionic selectivity of cells,[7,8] and the characteristics of membranes for reverse osmosis processes.[9] It is the purpose of this paper to explore certain aspects of the nature and identity of the sites of these interactions; we will propose, for instance, that the C–N bond of N,N-disubstituted amides is also an active binding site and that, consequently, the mesomerism of the peptide linkage[10] is significantly shifted in the presence of hydrogen donors such as water, alcohol, and chloroform (see eq A).

As model substances for our work we have chosen poly(1-vinyl-2-pyrrolidinone), abbreviated PVP (see

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