changing the LF to CT emission intensity ratios owing to changes in the relative populations in each state; (2) direct solvent effects on photosolvation rates and nonradiative decay rates. The latter effects, especially with regard to the substitution rate k_{Cl}, appear to be more important in determining photoreaction quantum yields. Clearly the enhanced photosolvation quantum yield of $IrCl_2(bpy)_2^+$ in water relative to the nonaqueous solvents results from larger increases in k_{Cl} than in k_n. The ability of the solvent to stabilize the developing charge separation along the Ir(III)---Cl^- bond appears to correlate with the rate of photosolvation, consistent with a dissociative or dissociative interchange mechanism from the LF es. However, because of the absence of any clear deuterium isotope effect on the excited-states lifetimes and photosolvation rates in the reactive solvents, we cannot presently assert whether photosolvation and nonradiative deactivation are competing processes of the emitting LF excited state rather than competitive deactivation modes of an intermediate or hot ground-state species formed from the LF state.

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Pressure Effect on Rate and Equilibrium Constants of Reversible Anionic σ-Complex Formation between Polynitroaromatics and Lyate Ions of Water and Methanol

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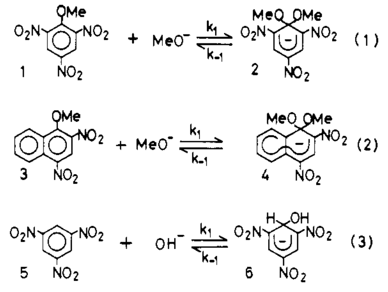
Abstract: The kinetics of the following reversible anionic σ-complex formation reactions was studied by the high-pressure stopped-flow method up to 1500 bar at 25 °C: 2,4,6-trinitroanisole + $MeO^- \rightleftharpoons$ **2** in methanol, 1-methoxy-2,4-dinitronaphthalene + $MeO^- \rightleftharpoons$ **4** in methanol, and 1,3,5-trinitrobenzene + $OH^- \rightleftharpoons$ **6** in water. The rate constants for complex formation in methanol increased with pressure, while that in water decreased slightly. Interestingly, the rate constants of reversion to reactants increased with pressure in all cases. It was concluded from the consideration of the volume of activation that the electronic charge is not completely delocalized into the ring system in the transition state and that local electrostriction in the vicinity of the nucleophile is still reflected in the volume. The pressure effect on the equilibrium constant for formation of **4** leads to a reaction volume consistent with that determined by the kinetic studies. The pressure-induced spectral red shifts of **2** and **4** are intelligible in terms of the density change of the solvent and the electronic character of the excited states. The anomalous pressure effect on the formation of **6** was explainable in terms of the strong solvation of OH^- in water.

The anionic σ complexes between polynitroaromatic substances and nucleophilic ions such as hydroxide and alkoxide ions have received much attention since the complex is often a reaction intermediate in nucleophilic substitutions.[1-5] The spectroscopic characteristics of these complexes have been extensively studied by means of electronic and NMR spectra,[5,6] and voluminous studies have been reported on the kinetics of their reversible formation reaction and further transformation. It is found[5,6] that their stability and reactivity are strongly dependent on the nucleophile as well as the solvent; however, the role of the solvent in each reaction step seems to remain uncertain.

High-pressure kinetic studies of chemical reactions in solution are recognized to give very important information about the reaction dynamism and the role of the solvent in activation.[7] To date, the usual high-pressure techniques for thermal reactions have been restricted to these with half-lives longer than ca. 20 min, since it takes some time after compression to attain thermal equilibrium. We have developed a high-pressure stopped-flow method which is a different type from Heremans'[8] and succeeded in following reactions as fast as several milliseconds up to 1500 bar,[9,10] so it became possible to examine irreversible reactions or observable transient intermediate. This paper deals with the volume profile of some anionic σ-complex formations (1)-(3).



Experimental Section

Materials. 2,4,6-Trinitroanisole (**1**) was synthesized from 1-chloro-2,4,6-trinitrobenzene (**7**) and sodium methoxide in methanol. Into 30 mL of methanol was dissolved 5 g of **7**, and 4.8 g of 28% NaOMe in methanol was added, and then the mixture was refluxed for 4 h. After being cooled at room temperature, the mixture was neutralized by means of 0.5 N aqueous H_2SO_4 solution. The precipitate was recrystallized several times from methanol; mp 68.0 °C. 1-Methoxy-2,4-dinitronaphthalene (**3**) was synthesized according to the procedure of Fendler et al.[11] and recrystallized from methanol; mp 98.5 °C. Commercially obtained 2,4,6-trinitrobenzene (**5**) was recrystallized several times from methanol; mp

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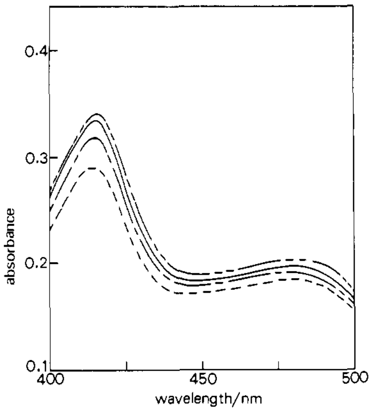


Figure 1. Electronic absorption spectra of **2** at several pressures: (---) 1 bar; (---) 500 bar; (—) 1000 bar; (----) 1500 bar. $[\mathbf{1}]_0 = 1.4 \times 10^{-5}$ M, $[MeO^-]_0 = 1.0$ mM.

122.5 °C. Reagent solution of sodium methoxide was prepared by dissolving fresh sodium metal in methanol under a nitrogen atmosphere; the concentration was determined by titration with standard HCl solution. Anhydrous sodium perchlorate was prepared by dehydration of $NaClO_4 \cdot 2H_2O$ at 130 °C under vacuum for 12 h. Methanol was distilled according to the standard procedure.

Equilibrium Measurements. The equilibrium constant for the formation of **4** was determined from its electronic absorption spectrum at high pressure by using a Drickamer-type of high-pressure vessel[12] made of maraging steel. The pressure was measured with a manganin-wire coil calibrated with a Heise bourdon gage. The optical path length was around 6 mm; it was precisely determined at each run by comparing the absorbance at 1 bar with that measured separately with a 10-mm cuvette by a Shimadzu UV-200S spectrophotometer. High-pressure spectrophotometry was carried out by use of a Union Giken RA-405 single-beam spectrophotometer equipped with a data processor (Union Giken System-71), which made it possible to correct drift or instability of the apparatus by a divided light path.

Since equilibrium 1 lies far to the right-hand side, the equilibrium constant could not be quantitatively determined. Complex **6** undergoes an irreversible reaction, so that static measurement of reaction 3 was also impossible.

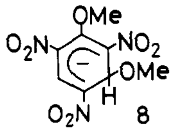
Kinetic Experiment. The reaction rate of **1** with methoxide ion was followed by means of a high-pressure stopped-flow apparatus of the pressure-drive type; the details have been published elsewhere.[9] It is satisfactorily applicable to reactions as slow as several seconds or more. The reactions of **3** with methoxide and of **5** with hydroxide were pursued with an improved high-pressure stopped-flow apparatus,[10] which was enough for reactions from several milliseconds to a few minutes. Succeeding reactions of **2** and **4** did not occur, but that of **6** did to produce the corresponding phenol though the latter was negligibly slow in comparison with the rate of attainment of equilibrium 3.

Each reaction was studied with the nucleophilic ion in a large excess over the polynitroaromatic compounds, so that a pseudo-first-order treatment could be applied. The time dependence was measured spectrophotometrically at the maxima of the anionic complexes. The optical path length was always 10 mm.

In all measurements, the temperature was kept at 25 ± 0.1 °C by circulating thermostated fluid around the high-pressure vessels.

Results

Spectral and Equilibrium Measurement. The reaction of **1** with methoxide ion is known to produce two complexes: **2** and **8**.[5d,6]



8

The latter, however, proceeds to formation prior to **2** in methanol, and its rate can barely be followed by a stopped-flow temperature-jump technique,[13] and finally, **2** is much more stable than **8**; in this study, we therefore ignore the formation of **8**. Moreover, a second (1:2) adduct appears when the methoxide ion is in excess over the substrate by a factor of more than 3500.[14] To avoid this complication, we chose experimental conditions in each case such that only the 1:1 complex could be produced.

Table I. Comparison of Absorbance Ratio A_1/A_p with Specific Volume Ratio V_p/V_1 of Complex **2** in Methanol at 25 °C

	pressure/bar					
	1	300	600	900	1200	1500
A_1/A_p	1.000	0.967	0.954	0.929	0.915	0.903
$V_p/V_1{}^a$	1.000	0.967	0.949	0.931	0.915	0.901

[a] Reference 25.

Table II. Equilibrium Constant K and Molar Absorption Coefficient ϵ of Complex **4** in Methanol at Several Pressures (25 °C)

	pressure/bar					
	1	300	600	900	1200	1500
$\epsilon/10^4$ M^{-1} cm^{-1}	2.57	2.56	2.53	2.45	2.46	2.44
K^a/M^{-1}	177	181	184	209	204	216

[a] Experimental error is ±2.5%.

Figure 1 shows the absorption spectra of **2** at several pressures with MeO^- in excess at ca. 1 mM. The increase of absorption intensity is expected to result from two factors: the increase of concentration of absorbing species due to compression and the shift of equilibrium. Table I gives the absorbance ratio A_1/A_p and the specific volume ratio V_p/V_1, where subscripts 1 and p refer to 1 and p bar, respectively; they appear to be equal. This observation points out that equilibrium 1 is fairly in favor of **2**; indeed, there is a report[15] that the equilibrium constant K $(=k_1/k_{-1})$ is as large as 1.7×10^4 M^{-1}. Our present kinetic data also result in a very small value of k_{-1}, as will be described later. By taking into account that K is of the order of 10^4 and that the molar absorption coefficient[14] ϵ is around 2.4×10^4, we expected that a measurement with conditions of ca. 10^{-4} M MeO^- and 10^{-5} M **1** would make it possible to determine the pressure effect on K. Under these conditions, however, the absorbance of the mixture in the high-pressure vessel decreased gradually with time, and so we were unable to determine the reliable values. In spite of the uncertainty, we qualitatively found from the absorbance within a short interval that K seemed to increase with pressure, suggesting that the reaction volume is negative as will be discussed in the later section.

Figure 1 shows that both absorption maxima at around 410 and 480 nm shift though slightly but obviously to longer wavelengths with increasing pressure. The increase of the absorbance of **4** by pressure was more than the increase of molar concentration due to compression. When $[MeO^-]_0 >> [\mathbf{3}]_0$, the equilibrium constant K is obtained by the Scott equation (4),[16] where l is the

$$\frac{[\mathbf{3}]_0[MeO^-]_0 l}{A} = \frac{1}{\epsilon}[MeO^-]_0 + \frac{1}{K\epsilon} \qquad (4)$$

optical path length, A the absorbance of **4** at 495 nm, and ϵ the molar absorption coefficient, and molar concentrations are corrected for compression. At each pressure, the plot of $[\mathbf{3}]_0[MeO^-]_0 l/A$ against $[MeO^-]_0$ gave a straight line, from which ϵ and K were determined. Table II summarizes the numerical values calculated by the least-squares method. The value of K at 1 bar is a little smaller than that given by Fendler et al.[11] A slight red shift of the maxima by pressure was observed in this system also.

Reaction Rate. The observed first-order rate constant k_{obsd} under the pseudo-first-order condition can be expressed by eq 5.

$$k_{obsd} = k_1[Nu^-]_0 + k_{-1} \qquad (5)$$

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(13) C. F. Bernasconi, *J. Am. Chem. Soc.*, **93**, 6975 (1971).

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Table III. Rate Constant k_1 for the Formation of Complex **2** in Methanol at Several Pressures (25 °C)

pressure/bar	1	250	500	750	1000
k_1/M^{-1} s^{-1}	15.4 ± 0.4	16.2 ± 0.4	16.8 ± 0.4	17.4 ± 0.4	18.1 ± 0.4

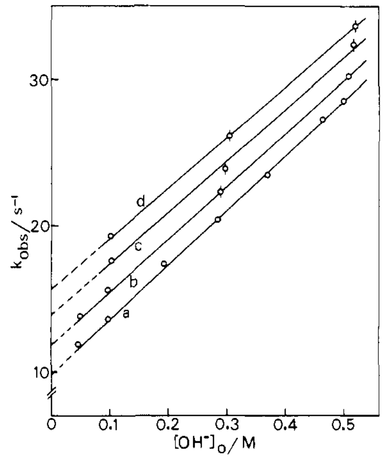

Figure 2. Dependence of k_{obsd} on hydroxide ion concentration in the **5** + OH^- system in water at 25 °C: a, 1 bar; b, 500 bar; c, 1000 bar; d, 1500 bar.

For reaction 1, k_{obsd} was determined at the concentrations of ca. 3 × 10^{-5} M of **1** and 1–6 mM of MeO^-. The plot of k_{obsd} against $[MeO^-]_0$ gave a straight line passing near the origin; this is evidently so because the equilibrium constant is large and k_{-1} negligibly small. We did not find any effect of ionic strength by the addition of $NaClO_4$. The second-order rate constant k_1 is given in Table III.

For reaction 2, we monitored the rate at 495 nm and determined k_{obsd} over the concentration range of (2.5–5.0) × 10^{-5} M of **3** and 2.9–11.5 mM of MeO^-. Both k_1 and k_{-1} were calculated according to eq 5 and summarized in Table IV. The values of k_1, k_{-1}, and K at 1 bar are in good agreement with those of Fendler et al.[11]

Stopped-flow traces for reaction 3 in aqueous solution at 435 nm also obey the first-order rate equation very well. The concentration range was (2.3–7.1) × 10^{-5} M of **5** and 0.10–0.50 M of OH^-. The observed first-order rate constants depend on $[OH^-]_0$ as shown in Figure 2. The numerical values of k_1 and k_{-1} are given in Table IV. Bernasconi studied the reactions of trinitrobenzene and its derivatives with lyate ions of water and alcohols at 1 bar;[13,17] the present results agree well with his. At concentrations of OH^- higher than 0.6 M the electronic spectrum of the mixture and the stopped-flow trace indicated the formation of the 1:2 adduct; this was not investigated further.

Discussion

Spectral Shift. Pressure-induced spectral shifts can be understood in terms of the change in electrostatic properties of the solvent; there are many examples of that.[18] McRae[19] introduced eq 6 which was generally applicable to the frequency shift in

$$\Delta\nu = (AL + B)\frac{n^2 - 1}{2n^2 + 1} + C\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 1}\right] + F\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right]^2 \quad (6)$$

transfer from gas phase to solution. In this equation A, B, C, and

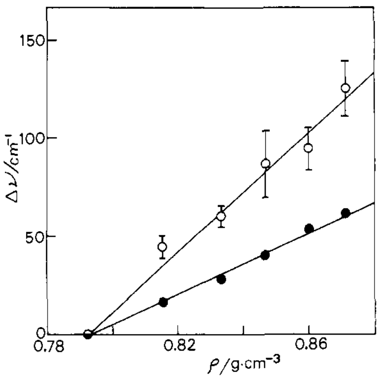

Figure 3. Pressure-induced frequency shifts of complexes **2** and **4**: (○) **2**; (●) **4**.

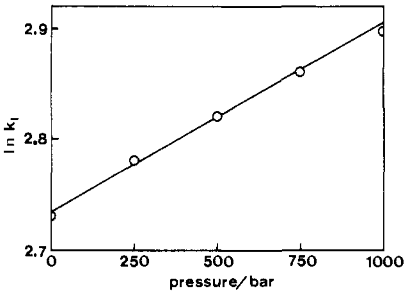

Figure 4. Pressure dependence of k_1 in the **1** + MeO^- system in methanol at 25 °C.

F are constants characteristic of a particular transition of a given solute, n is the refractive index of the solvent, and D is its dielectric constant. The first term with the constant A and the weighted mean wavelength L[19] represents the induced dipole–induced dipole interaction, the second term with B the solute dipole–solvent-induced dipole interaction, the third term the dipole–dipole, and the last term the solvent dipole–solute-induced dipole interaction. For nonpolar solvents, the bracketed terms approximate zero, and the McRae equation then reduces to that given by Bayliss.[20] For polar solvents, Robertson's modified eq 7[21] by combination of the

$$\Delta\nu = A'\frac{n^2 - 1}{2n^2 + 1} + C'\rho + F'\rho^2 \quad (7)$$

Debye and Lorenz–Lorentz equations[22] gives an expression as a function of solvent density ρ, where A' is the constant of the term $AL + B$ in eq 6 and C' and F' are constants C and F of eq 6 modified by a constant introduced by the density form in use in the Debye and Lorenz–Lorentz equations. Equation 7 predicts the pressure-induced frequency shift for a polar solute in a polar medium as well as for a nonpolar solute in a nonpolar solvent. Variation of $(n^2 - 1)/(2n^2 + 1)$ with pressure is much smaller than the change of ρ, and $\Delta\nu$ is expected to change almost linearly with ρ. Figure 3 shows the results of pressure-induced frequency shifts of **2** and **4**, which support the above description. The red shift for **2** is larger than for **4**; this results from the difference in the electronic distribution in the excited states. The electronic transition of **2** is assigned to that from the electronically delocalized ground state to the excited one in which the electron densities are more enhanced at the NO_2 groups.[23] Accordingly, the excited state is more highly solvated than the ground state, which will lead to the red shift by pressure. The electronic charge in the

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(17) C. F. Bernasconi, *J. Am. Chem. Soc.*, **92**, 4682 (1970).

(18) For example see T. Nakayama, *Rev. Phys. Chem. Jpn.*, **49**, 25 (1979) and literatures cited therein.

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(21) W. W. Robertson and A. D. King, Jr., *J. Chem. Phys.*, **34**, 1511 (1961).

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(23) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).

Table IV. Rate Constants k_1 and k_{-1} and Equilibrium Constant K for Complex Formations of 4 and 6 at Several Pressures (25 °C)

	complex 4			complex 6		
pressure/bar	k_1/M^{-1} s^{-1}	10^2k_{-1}/s^{-1}	K/M^{-1}	k_1/M^{-1} s^{-1}	k_{-1}/s^{-1}	K/M^{-1}
1	0.89 ± 0.01	0.39 ± 0.01	228 ± 3	37.4 ± 0.5	9.8 ± 0.1	3.8 ± 0.2
500	1.10 ± 0.02	0.47 ± 0.01	234 ± 4	35.8 ± 0.5	11.8 ± 0.2	3.0 ± 0.2
1000	1.30 ± 0.02	0.55 ± 0.01	236 ± 4	35.0 ± 0.4	13.9 ± 0.2	2.5 ± 0.2
1500	1.56 ± 0.02	0.65 ± 0.01	240 ± 4	34.4 ± 0.4	15.7 ± 0.2	2.2 ± 0.2

Table V. Kinetic and Equilibrium Parameters of Anionic σ-Complex Formation at 25 °C and 1 bar

	2 in MeOH		4 in MeOH		6 in H_2O	
k_1/M^{-1} s^{-1}	15.4 ± 0.4	(17.3[a])	0.89 ± 0.01	(0.95[b])	37.4 ± 0.5	(37.5[c])
k_{-1}/s^{-1}		(10^{-3} [a])	3.9 × 10^{-3}	(3.95 × 10^{-3} [b])	9.8 ± 0.1	(9.8[c])
K/M^{-1}		(1.7 × 10^4 [a])	228 ± 2	(230[b])	3.8 ± 0.2	(3.73[c])
$\Delta V_1^‡$/cm^3 mol^{-1}	−7.2 ± 0.8		−13.2 ± 1.2		1.1 ± 1.0	
$\Delta S_1^‡$/cal mol^{-1} K^{-1}		(−9.4 ± 2.0[a])		(−17 ± 2[b])		(1.1 ± 2.7[c])
$\Delta V_{-1}^‡$/cm^3 mol^{-1}			−8.9 ± 1.0		−8.9 ± 1.2	
$\Delta S_{-1}^‡$/cal mol^{-1} K^{-1}		(−4.8 ± 2.0[a])		(−18 ± 2[b]		(−29.4 ± 2.7[c])
ΔV/cm^3 mol^{-1}	<0		−4.3 ± 2.2[d]	(−5.2 ± 1.3[e])	10.0 ± 2.2	
ΔS/cal mol^{-1} K^{-1}		(−4.6 ± 4.0[a])		(~0[b])		(30.5 ± 5.4[c])

[a] Reference 15. [b] Reference 11. [c] Reference 17. [d] Kinetic measurement. [e] Equilibrium measurement.

excited state of **4** is more delocalized into the aromatic system than in **2**, and so the pressure-induced red shift is diminished.

Pressure Effect on Rate and Equilibrium. From the results in Tables III and IV, the volumes of activation were determined by eq 8, which is derived from the expression of the rate constant

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^‡}{RT} + \Delta n^‡\kappa \tag{8}$$

on the basis of transition state theory.[24] $\Delta V^‡$ is the volume of activation, $\Delta n^‡$ is the difference in the number of molecules between the initial and transition state, κ is the compressibility of the solution, and R is the gas constant. The plots of ln k against pressure are shown in Figures 4, 5, and 6. From the slopes at 1 bar, the volumes of activation were calculated with $\Delta n^‡ = -1$ for the forward reaction and $\Delta n^‡ = 0$ for the reverse. The values of κ were calculated from the data of Skinner et al.[25] for methanol and those of Kell[26] for water. The values of $\Delta V^‡$ are summarized in Table V together with the other kinetic and equilibrium parameters. The reaction volume ΔV of formation of **4** was obtained both from direct measurement of pressure effect on K and from $\Delta V = \Delta V_1^‡ - \Delta V_{-1}^‡$. The plot of ln K against pressure is approximately a straight line, though the experimental points are scattered a little as seen from Table II. The equilibrium parameters determined by the different methods agree well.

Volumetric values generally (though not exactly) correlate with entropy changes; at least, the signs correspond. An interesting fact is that $\Delta V_{-1}^‡$ is negative for both **4** and **6** in spite of the bond breaking. The volume of activation mainly reflects structural ($\Delta V_s^‡$) and electrostrictive solvation change ($\Delta V_e^‡$) on going from the initial to the transition state. Since the unimolecular decomposing process is associated with the bond stretch of a C–O bond, $\Delta V_s^‡$ is positive with a magnitude of 2–8 cm^3/mol;[7] the negative value of ΔV_{-1} must therefore result from a greatly negative value of $\Delta V_e^‡$, *i.e.*, from an increase in electrostrictive solvation during activation. This consideration leads to the views that at the transition state, the electronic charge will be less delocalized in the ring system than is the case in the anionic σ complex and that the volume contraction due to the local electrostriction[27] in the vicinity of the RO (R = H or Me) group at the transition state is so large that the positive value due to the bond stretch is more than compensated. This explanation is consistent with the forward reaction; that is to say, at the transition state, electronic charge remains, for the most part, localized on the nucleophilic ion, and thus the contraction of the van der Waals distance between two reactants predominantly contributes to the volume of activation. The magnitudes of $\Delta V_1^‡$ for **2** and **4** are similar to those of many bimolecular reactions between neutral molecules.[7,24]

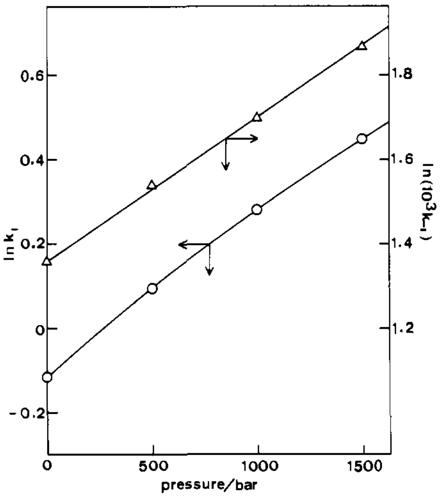

Figure 5. Pressure dependence of k_1 and k_{-1} in the **3** + MeO$^-$ system in methanol at 25 °C.

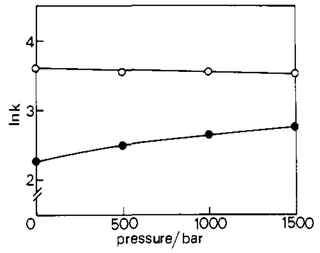

Figure 6. Pressure dependence of k_1 and k_{-1} in the **5** + OH$^-$ system in water at 25 °C: (○) k_1; (●) k_{-1}.

The anomaly that $\Delta V_1^‡$ is positive in reaction 3 in spite of the bond-forming process is probably brought about by the peculiarly strong solvation of hydroxide ion in water, which is reflected in the entropy of dissolution.[28] In aqueous solution, the expansion of the solvation shell around a hydroxide ion upon activation may

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(27) E. Whalley, *Adv. Phys. Org. Chem.*, **2**, 93 (1964).

(28) R. W. Gurney, "Ionic Processes in Solution", Dover Publications, New York, 1953, Chapter 10.

exceed the contraction due to the bond formation. This anomaly in $\Delta V_1^\ddagger$ is also consistent with the anomalously high $\Delta S_1^\ddagger$ found in the same reaction.[17] More extensive volumetric studies of anionic complexes of polynitroaromatics, for example, with multivalent nucleophilic ions and with a series of lyate ions may support this explanation.

Acknowledgment. The present work was supported by the Research Grant-in-Aid from the Ministry of Education (No. 454123).

A Kinetic Study of Sensitized 9,10-Dibromoanthracene Fluorescence Produced by Energy Transfer from Triplet Ketones. 1. Acetophenone as Donor

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Abstract: The decay of the fluorescence intensity of degassed solutions of 9,10-dibromoanthracene (DBA) and acetophenone, upon excitation in the absorption band of the ketone, was studied by the time-correlated single-photon-counting method. The decay curves are described by double-exponential functions. For each solution, the prompt intensity component is due to direct excitation of DBA, and the slow component is the result of energy transfer from triplet acetophenone. The rate constant k_{ET} of this energy-transfer process is obtained from linear plots of the rate of the slow decay component vs. DBA concentration; the values of k_{ET} are 7.0×10^9 M^{-1} s^{-1} in benzene and in cyclohexane and 1.1×10^{10} M^{-1} s^{-1} in acetonitrile. Extrapolation of the same plots gives the rate of decay of triplet acetophenone in the absence of DBA in the particular solvent. The results agree well with the literature values. Knowing k_{ET}, the efficiency ϕ_{TS} of the overall triplet-singlet energy-transfer process is obtained from the analysis of each double-exponential decay curve, using the prompt component as internal standard. The values of ϕ_{TS}, 0.118, 0.102, and 0.126 in benzene, cyclohexane, and acetonitrile, respectively, show that ϕ_{TS} is quite insensitive to the solvent, with triplet acetophenone as donor. The value of ϕ_{TS} in benzene is consistent with the result of photostatic experiments in that solvent. The mechanism of this TS energy transfer to DBA is discussed, mainly in terms of a collisional triplet-triplet transfer to a higher triplet of DBA, followed by isc (isc = intersystem crossing) to the (lower) S_1 state. If this interpretation is correct, the efficiency of isc T_2 (or T_3) to S_1 is high, $\gtrsim 0.12$. DBA is shown to be a sensitive probe for triplet ketones.

Introduction

The population of the excited singlet state of 9,10-dibromoanthracene (DBA) via energy transfer from triplet ketones is an example of an overall spin-forbidden (T-S) process. It may, however, involve the intermediacy of a higher excited state of DBA, resulting from a triplet-triplet transfer, followed by intersystem crossing to populate S_1. This is one of many interesting aspects of a process which is surprisingly efficient and lends itself well to quantitative kinetic study.

Attention was first called to DBA as an acceptor of triplet energy by Vassil'ev[2] in the course of his studies of the chemiluminescence accompanying autoxidation processes. He observed that the addition of DBA to solutions presumed to contain chemically excited triplet carbonyls produced an intense emission which matched spectroscopically the fluorescence of DBA. This emission could be dramatically brighter than the very weak luminescence emitted by the triplet carbonyls themselves. Vassil'ev interpreted this phenomenon as the result of a T-S energy-transfer process rendered more efficient—i.e., less spin forbidden—by the presence of the bromine atoms in the acceptor molecule.

If the efficiency of this T-S process were known with some accuracy and if it were independent of the nature of the carbonyl donor and solvent, a useful tool would be at hand for the investigation of reactions suspected of generating triplet state products.[3] Unfortunately, however, there is a discrepancy of more than an order of magnitude between the two reported values of ϕ_{TS}, defined as $\phi_{TS} = k_{TS}/k_{ET}$ (where k_{TS} is the rate constant for the process resulting in the formation of excited singlet DBA and k_{ET} is the sum of the rate constants for all the bimolecular quenching processes involving DBA). With triplet acetophenone as the donor in benzene solution, Vassil'ev et al. reported $k_{TS} = 3.8 \times 10^8$ M^{-1} s^{-1} and $\phi_{TS} = 0.027$, assuming $k_{ET} = 1.4 \times 10^{10}$ M^{-1} s^{-1}. For the same donor, but with 9,10-diphenylanthracene as the acceptor, these authors reported values of ϕ_{TS} 2 orders of magnitude smaller.[2]

However, from an almost contemporary but independent photophysical study of the same acetophenone-DBA system, Berenfel'd et al.[4] reported the much higher value of $\phi_{TS} = 0.3$. These authors excited acetophenone in degassed benzene solution containing DBA and measured the effect of DBA on (1) the rate of decay of the sensitized fluorescence of DBA following 10^{-7}-s pulsed excitation and (2) the efficiency of this sensitized fluorescence of DBA under photostationary conditions. The first set of experiments gave $k_{ET} = (5 \pm 0.5) \times 10^9$ M^{-1} s^{-1}; from the second set, they obtained $\phi_{TS} = 0.3$, hence $k_{TS} = 1.5 \times 10^9$ M^{-1} s^{-1}, thus a significantly higher value than that of Vassil'ev et al. Unfortunately this paper presented only scant experimental information, in spite of the problems attached to quantitative fluorescence measurements in highly absorbing solutions. Selective photoexcitation of acetophenone in the presence of DBA is very difficult to achieve. Thus in static photosensitization experiments,

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