

# Kinetic and Equilibrium Study of the Interaction of *N,N*-Dipropyl-2,6-dinitro-4-(trifluoromethyl)aniline with Hydroxide Ion in Water-Dimethyl Sulfoxide Solutions<sup>1</sup>

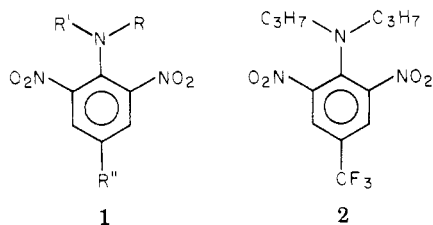
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In the presence of potassium hydroxide in water-Me<sub>2</sub>SO mixtures, the title compound **2** gives the 1:1  $\sigma$  complex by addition of hydroxide ion to the unsubstituted ring position; kinetic and equilibrium data are reported. A linear relationship between  $\log k_1$ ,  $\log k_{-1}$ , and  $\log K_1$  and the molar fraction of Me<sub>2</sub>SO is found. In Me<sub>2</sub>SO-water (40%, v/v), the kinetic and equilibrium measurements suggest that the dianion arising from the ionization of the hydroxyl group of the adduct **3** is formed.

Dinitroanilines **1**, with a number of substituents on the aromatic ring and on the nitrogen, constitute an important group of plant-growth regulators, but their mechanism of action is not known.<sup>3</sup>



Since all these compounds bear in common the electron-deficient aromatic ring, it was suggested<sup>4</sup> that their biological activity might be derived from their ability to form Meisenheimer complexes<sup>5</sup> with nucleophiles in the plant cells. This suggestion is based on the very low activity of compounds where R'' = COOH or NH<sub>2</sub>, which do not readily form Meisenheimer intermediates, and the fact that picramide and *N,N*-disubstituted picramides form stable Meisenheimer complexes.<sup>6</sup>

It was of interest to investigate the kinetic and thermodynamic properties of the interactions of these compounds with nucleophiles, in particular hydroxide, thiolate anions, and amines, in order to get a better understanding of their biological behavior.

We report here the interaction of *N,N*-dipropyl-2,6-dinitro-4-(trifluoromethyl)aniline (trifluralin) (**2**), which is a commonly used plant-growth regulator,<sup>7</sup> with hydroxide ion.

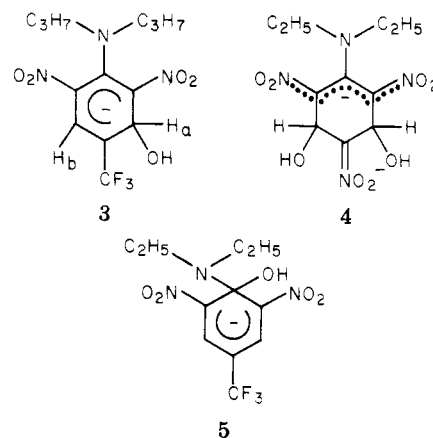
## Results and Discussion

**Spectroscopic Studies.** The addition of potassium hydroxide to a solution of **2** in Me<sub>2</sub>SO-water of varying Me<sub>2</sub>SO content (40–80%, v/v) results in the development of two absorption bands,  $\lambda = 430$  and 340 nm, which increase in intensity with the concentration of hydroxide.

The spectra recorded at different OH<sup>-</sup> concentrations give good isosbestic points in 60–80% Me<sub>2</sub>SO (Figure 1) but are not well defined in 40 and 50% Me<sub>2</sub>SO.

We have measured the <sup>1</sup>H NMR spectrum to determine the structure of the colored compound formed.

The spectrum of **2** in Me<sub>2</sub>SO shows one single absorption in the aromatic region at  $\delta$  8.40. After the addition of 1 equiv of KOH and enough water to make the composition of the solvent 80% in Me<sub>2</sub>SO, two new peaks appear at  $\delta$  5.84 and 7.50, each of which integrated for one proton. They can be attributed to H<sub>a</sub> and H<sub>b</sub> in **3** by comparison



with similar compounds.<sup>4,5c</sup> The absorption due to the parent **2** only disappears completely after the addition of 2 equiv of KOH.

The spectrum of diethylpicramide under identical experimental conditions shows an absorption at  $\delta$  6.09, corresponding to the ring protons in **4**, in agreement with data reported by Crampton.<sup>6c</sup> Thus we could not find evidence for the formation of the 1:2  $\sigma$  complex of **2** under these conditions. Solubility reasons preclude investigation in solvents of lower Me<sub>2</sub>SO content.

In order to confirm that there was no addition to C-1, we prepared a solution of **2** in 80% Me<sub>2</sub>SO containing 10<sup>-2</sup> M KOH and then added it to a 1 M HCl solution. If complex **5** had been formed it would have yielded the phenol upon acidification, since it would be protonated on nitrogen, and the amine would leave very fast.<sup>8</sup>

**Equilibrium Determinations.** The results presented above suggest that the reaction of **2** with hydroxide ion in Me<sub>2</sub>SO-water can be described by eq 1.



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(3) (a) F. M. Ashton and A. I. Crafts, "Mode of Action of Herbicides", Wiley-Interscience, New York, 1973, p 504; (b) S. J. Parke and O. F. Soper, *Weed Sci.*, **25**, 79 (1977).

(4) R. C. Hall and C. S. Giam, *J. Agric. Food Chem.*, **22**, 461 (1974).

(5) For recent reviews on Meisenheimer complexes, see: (a) E. Bunzel, A. R. Norris, and K. E. Russell, *Q. Rev., Chem. Soc.*, **22**, 123 (1968); (b) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969); (c) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(6) (a) Y. D. Grudtsyn and S. S. Gitis, *J. Org. Chem. USSR (Engl. Transl.)*, **11** (12), 2616 (1975); (b) M. R. Crampton, *J. Chem. Soc. B*, 1208 (1968); (c) M. R. Crampton and V. Gold, *ibid.*, 893 (1966).

(7) W. A. Gertner, *Weed Sci.*, **18**, 629 (1970).

(8) C. F. Bernasconi, R. H. de Rossi, and C. L. Gehriger, *J. Org. Chem.*, **38**, 2838 (1973).

Table I. Interaction of 2 with Potassium Hydroxide in Water-Dimethyl Sulfoxide at 25 °C

[KOH], M	$A - A_0^a$	$(A - A_0)_{\text{calcd}}$
0.098 (30%) <sup>b,c</sup>		
0.1	0.016	
0.2	0.031	
0.4	0.066	
0.6	0.110	
0.8	0.150	
1.0	0.190	
0.141 (40%) <sup>b,d</sup>		
0.150	0.044	0.040 <sup>e</sup>
0.260	0.108	0.108 <sup>e</sup>
0.360	0.169	0.183 <sup>e</sup>
0.470	0.251	0.265 <sup>e</sup>
0.571	0.327	0.333 <sup>e</sup>
0.672	0.380	0.392 <sup>e</sup>
0.773	0.469	0.442 <sup>e</sup>
0.890	0.514	0.489 <sup>e</sup>
1.008	0.544	0.527 <sup>e</sup>
0.199 (50%) <sup>b,f</sup>		
0.0513	0.100	0.100 <sup>g</sup>
0.115	0.177	0.182 <sup>g</sup>
0.179	0.261	0.260 <sup>g</sup>
0.244	0.277	0.313 <sup>g</sup>
0.308	0.357	0.356 <sup>g</sup>
0.372	0.433	0.390 <sup>g</sup>
0.436	0.425	0.419 <sup>g</sup>
0.500	0.454	0.443 <sup>g</sup>
0.268 (60%) <sup>b,h</sup>		
0.00986	0.087	0.088 <sup>i</sup>
0.015	0.125	0.125 <sup>i</sup>
0.029	0.233	0.203 <sup>i</sup>
0.058	0.315	0.308 <sup>i</sup>
0.104	0.395	0.398 <sup>i</sup>
0.200	0.485	0.483 <sup>i</sup>
0.505	0.520	0.562 <sup>i</sup>
0.355 (70%) <sup>b,j</sup>		
0.003	0.179	0.183 <sup>k</sup>
0.0058	0.261	0.271 <sup>k</sup>
0.0099	0.340	0.345 <sup>k</sup>
0.015	0.397	0.396 <sup>k</sup>
0.029	0.472	0.461 <sup>k</sup>
0.058	0.527	0.506 <sup>k</sup>
0.104	0.534	0.528 <sup>k</sup>

<sup>a</sup> Measured absorption minus absorption of 2 in pure solvent. <sup>b</sup> Mole fraction of 2 (% Me<sub>2</sub>SO, v/v). <sup>c</sup> [2]<sub>0</sub> = 3.18 × 10<sup>-5</sup> M, μ = 1 M (KCl as compensating electrolyte), ε = 20 000, ε<sub>2</sub> = 2500. <sup>d</sup> [2]<sub>0</sub> = 4.97 × 10<sup>-5</sup> M, μ = 1 M (KCl as compensating electrolyte). <sup>e</sup> Calculated from eq 8 with ε<sub>3</sub> - ε<sub>2</sub> = 14 600 and K<sub>1</sub>K<sub>6</sub> = 2.6 M<sup>-2</sup>. <sup>f</sup> [2]<sub>0</sub> = 4.18 × 10<sup>-5</sup> M. <sup>g</sup> Calculated from eq 2 with ε<sub>3</sub> - ε<sub>2</sub> = 17 400 and K<sub>1</sub> = 3.11 M<sup>-1</sup>. <sup>h</sup> [2]<sub>0</sub> = 3.60 × 10<sup>-5</sup> M<sup>-1</sup>. <sup>i</sup> Calculated from eq 2 with ε<sub>3</sub> - ε<sub>2</sub> = 17 500 and K<sub>1</sub> = 16.5. <sup>j</sup> [2]<sub>0</sub> = 3.18 × 10<sup>-2</sup> M. <sup>k</sup> Calculated from eq 2 with ε<sub>3</sub> - ε<sub>2</sub> = 17 600 and K<sub>1</sub> = 162 M<sup>-1</sup>.

In order to determine K<sub>1</sub>, we measured the optical density at 430 nm of solutions of 2 at different KOH concentrations (Table I). Since under all our experimental conditions [OH<sup>-</sup>] ≫ [2]<sub>0</sub> and 2 absorbs considerably at this wavelength (ε<sub>2</sub> 2600–3000), the measured optical density can be expressed by eq 2, where A is the measured absorption and A<sub>0</sub> is the absorption of 2 in the pure solvent.

$$A - A_0 = \frac{K_1[\text{OH}^-]_0}{1 + K_1[\text{OH}^-]_0}(\epsilon_3 - \epsilon_2)[2]_0 \quad (2)$$

A plot of the left-hand side of eq 2 vs. [OH<sup>-</sup>] should curve down and eventually level off at high OH<sup>-</sup> concentration. An inversion plot according to eq 3 should give

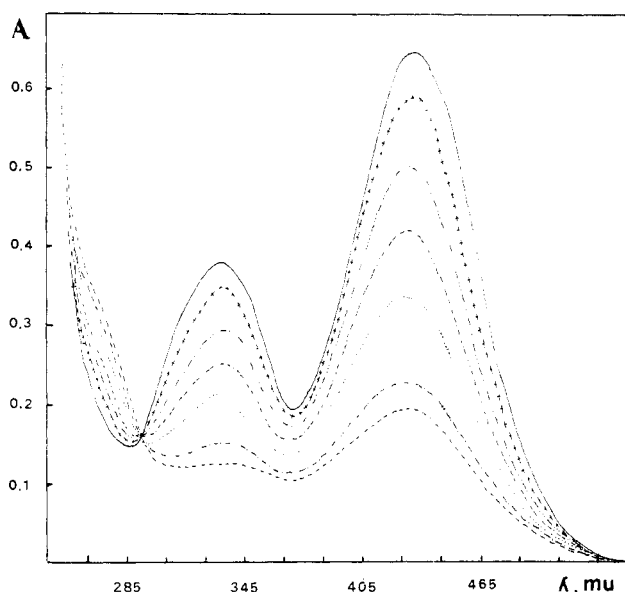


Figure 1. Absorbance of 2 in Me<sub>2</sub>SO-H<sub>2</sub>O (60%) at various potassium hydroxide concentrations ([2]<sub>0</sub> = 3.18 × 10<sup>-5</sup> M): (---) 9.9 × 10<sup>-3</sup> M, (---) 1.5 × 10<sup>-2</sup> M, (---) 2.9 × 10<sup>-2</sup> M, (-----) 5.8 × 10<sup>-2</sup> M, (---) 0.10 M, (+) 0.2 M, (—) 0.5 M.

Table II. Kinetic and Equilibrium Data for the Interaction of Potassium Hydroxide with 2

Me <sub>2</sub> SO <sup>a</sup>	K <sub>1</sub> , <sup>b</sup> M <sup>-1</sup>	K <sub>1</sub> , <sup>c</sup> M <sup>-1</sup>	10 <sup>2</sup> k <sub>11</sub> , <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	10 <sup>2</sup> k <sub>-1</sub> , <sup>e</sup> s <sup>-1</sup>
0	0.031 <sup>d</sup>		1.53 <sup>d</sup>	36.8 <sup>d</sup>
0.098	0.287 <sup>e</sup>			11.9
0.141		0.970	9.00	9.28 <sup>f</sup>
		(0.947)		(9.5) <sup>g</sup>
0.199	3.11	3.84	19.1	4.97
0.268	16.6	17.5	45.8	2.62
0.355	162	254	199	0.784
0.483		2475	656	0.265

<sup>a</sup> Mole fraction of Me<sub>2</sub>SO. <sup>b</sup> Spectrophotometric. <sup>c</sup> Kinetic. <sup>d</sup> Extrapolated, Figure 2. <sup>e</sup> Calculated from optical density measurements with ε<sub>3</sub> = 20 000. <sup>f</sup> Determined in pure solvent at μ = 1 M (KCl). <sup>g</sup> Value extrapolated from the plot of k<sub>obsd</sub> vs. [OH<sup>-</sup>].

(ε<sub>3</sub> - ε<sub>2</sub>)<sup>-1</sup> as intercept and [(ε<sub>3</sub> - ε<sub>2</sub>)K<sub>1</sub>]<sup>-1</sup> as slope. This is the usual Benesi-Hildebrand treatment.<sup>9</sup>

$$\frac{[2]_0}{A - A_0} = \frac{1}{\epsilon_3 - \epsilon_2} + \frac{1}{\epsilon_3 - \epsilon_2} \frac{1}{K_1} \frac{1}{[\text{OH}^-]_0} \quad (3)$$

In 50–70% Me<sub>2</sub>SO we found that our data nicely fit eq 3, and we could determine ε<sub>3</sub> and K<sub>1</sub> (Tables I and II).

In 80% Me<sub>2</sub>SO equilibrium 1 lies very much on the side of 3, even at very low OH<sup>-</sup> concentrations, and the plot of A - A<sub>0</sub> vs. [OH<sup>-</sup>] already levels off at [OH<sup>-</sup>] = 4 × 10<sup>-3</sup> M; thus we could not determine K<sub>1</sub> by this approach. On the other hand, in 30% Me<sub>2</sub>SO equilibrium 1 lies on the side of the reactants; i.e., K<sub>1</sub>[OH<sup>-</sup>] < 1, and the plot of A - A<sub>0</sub> vs. [OH<sup>-</sup>] is slightly curved upward. The measured equilibrium constant, K<sub>c</sub>, defined as in eq 4, was calculated

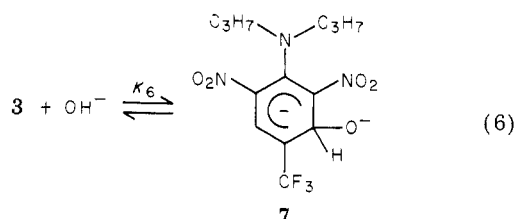
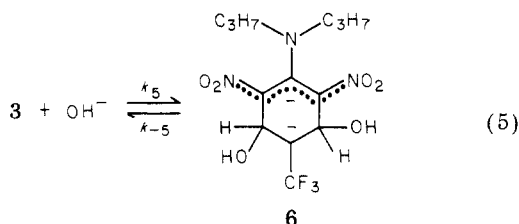
$$K_c = \frac{A - A_0}{([2]_0(\epsilon_3 - \epsilon_2) - (A - A_0))[\text{OH}^-]} \quad (4)$$

by using ε<sub>3</sub> 20 000, and it was found to increase slightly with OH<sup>-</sup> concentration. The number reported in Table II corresponds to the value extrapolated to zero OH<sup>-</sup> concentration.

(9) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949).

In 40% Me<sub>2</sub>SO a plot of 1/(A - A<sub>0</sub>) vs. [OH<sup>-</sup>]<sup>-1</sup> (not shown) is curved upward, whereas the plot (not shown) of 1/(A - A<sub>0</sub>) vs. [OH<sup>-</sup>]<sup>-2</sup> is linear.

This behavior might be explained by the formation of the 1:2 complex 6 as in eq 5 or by the ionization of 3 as in eq 6.



It is known that picramides are prone to add 2 mol of the nucleophile, forming 1:2  $\sigma$  complexes.<sup>10</sup> Although 6 could not be detected by NMR in 80% Me<sub>2</sub>SO, the more aqueous solvent and the high ionic strength could favor its formation.<sup>11</sup>

On the other hand, ionization of Meisenheimer complexes in the sense of eq 6 is precedented<sup>12</sup> and based on our kinetic results discussed below, and we believe that the second alternative (eq 6) can better explain our results.

If 7 is formed, the observed absorbance is given by eq 7, assuming that the extinction coefficients of 3 and 7 are the same.

$$A - A_0 = (\epsilon_3 - \epsilon_2) \frac{K_1[\text{OH}^-](1 + K_6[\text{OH}^-])}{1 + K_1[\text{OH}^-](1 + K_6[\text{OH}^-])} [2]_0 \quad (7)$$

The fact that the plot of 1/(A - A<sub>0</sub>) vs. [OH<sup>-</sup>]<sup>-2</sup> is linear indicates that  $K_6[\text{OH}^-] > 1$ , which simplifies eq 7 to eq 8.

$$A - A_0 = (\epsilon_3 - \epsilon_2) \frac{K_1 K_6 [\text{OH}^-]^2}{1 + K_1 K_6 [\text{OH}^-]^2} \quad (8)$$

From the slope and intercept of this plot (not shown) we calculate  $K_1 K_6 = 2.6 \text{ M}^{-2}$  and  $\epsilon_3 - \epsilon_2 = 14600$ . With these values we calculate A by using eq 8, and we found good concordance with the observed values (Table I). If we combine the value of  $K_1 K_6$  with  $K_1 = k_1/k_{-1}$  obtained from the kinetic results (Table II), we can calculate  $K_6 = 3.6 \text{ M}^{-1}$ , which is in good agreement with the value calculated from the kinetic results (see below). The coincidence between these two numbers is perhaps fortuitous since the condition that allows simplification of eq 7 into eq 8, i.e.,  $K_6[\text{OH}^-] > 1$ , is not quite fulfilled if  $K_6$  has this value.

The fact that no ionization is detected in solvents of higher Me<sub>2</sub>SO content may be due to the lower base concentration used and perhaps to a decrease in  $K_6$ , since the effect of solvent on  $K_6$  seems rather difficult to predict.<sup>13</sup>

**Kinetic Studies.** A solution of complex 3 was prepared in 90% Me<sub>2</sub>SO, and its rate of decomposition as a function

Table III.  
Kinetics of the Interaction of 2 with Potassium Hydroxide in Water-Dimethyl Sulfoxide Mixtures at 25 °C<sup>a</sup>

10 <sup>2</sup> [KOH], M	10 <sup>2</sup> k <sub>obsd</sub> , <sup>b</sup> s <sup>-1</sup>	10 <sup>2</sup> [KOH], M	10 <sup>2</sup> k <sub>obsd</sub> , <sup>b</sup> s <sup>-1</sup>
50% Me <sub>2</sub> SO			
1.0	5.24 ± 0.2	7.2	6.27 ± 0.18
2.0	5.39 ± 0.16	8.6	6.73 ± 0.20
2.5	5.61 ± 0.27	10.3	7.04 ± 0.30
4.2	5.43 ± 0.16	12.8	7.21 ± 0.20
5.5	6.18 ± 0.12	17.4	8.32 ± 0.80
6.4	6.36 ± 0.44	20.0	9.10 ± 0.50
60% Me <sub>2</sub> SO			
0.626	3.05 ± 0.01	5.80	5.15 ± 0.27
1.15	3.25 ± 0.01	11.6	8.22 ± 0.20
2.90	3.66 ± 0.03	17.4	10.5 ± 0.1
70% Me <sub>2</sub> SO			
0.145	1.07 ± 0.01	0.696	2.33 ± 0.03
0.290	1.23 ± 0.03	1.04	2.63 ± 0.02
0.464	1.74 ± 0.04	1.16	3.18 ± 0.10
0.609	2.06 ± 0.06		
80% Me <sub>2</sub> SO			
0.103	0.809 ± 0.37	0.503	3.67 ± 0.04
0.200	1.51 ± 0.04	0.652	4.39 ± 0.29
0.303	2.15 ± 0.08	0.800	5.50 ± 0.10
0.400	3.29 ± 0.04	1.01	6.83 ± 0.50

<sup>a</sup> [2]<sub>0</sub> = (3-5) × 10<sup>-5</sup> M. <sup>b</sup> Deviations reported are mean values of three or four determinations.

Table IV. Kinetics of the Interaction of 2 with Potassium Hydroxide in 40% Dimethyl Sulfoxide-Water at 25 °C

[KOH], M	10 <sup>2</sup> k <sub>obsd</sub> , <sup>b</sup> s <sup>-1</sup>	10 <sup>2</sup> k <sub>calcd</sub> , <sup>c</sup> s <sup>-1</sup>
0.0103	9.1 ± 0.1	9.21
0.0308	9.1 ± 0.2	8.71
0.0492	8.4 ± 0.1	8.35
0.0759	7.9 ± 0.1	7.92
0.101	7.51 ± 0.05	7.63
0.252	6.92 ± 0.03	6.94
0.454	7.5 ± 0.1	7.41
0.655	8.4 ± 0.1	8.47
0.840	9.6 ± 0.1	9.70
1.10	10.7 ± 0.2	10.9

<sup>a</sup> [2]<sub>0</sub> = 4.97 × 10<sup>-5</sup> M,  $\mu = 1 \text{ M (KCl)}$ . <sup>b</sup> Deviations reported are mean values for three or four determinations. <sup>c</sup> Calculated from eq 10 with  $k_1 = 9 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-1} = 9.5 \times 10^{-2} \text{ s}^{-1}$ , and  $K_6 = 4.1 \text{ M}^{-1}$ .

of potassium hydroxide and Me<sub>2</sub>SO concentration was measured.

In solutions containing 50-70% Me<sub>2</sub>SO the observed rate of decomposition of the complex is linearly related to the OH<sup>-</sup> concentration (Table III), indicating that the observed rate is given by eq 9.

$$k_{\text{obsd}} = k_1[\text{OH}^-] + k_{-1} \quad (9)$$

The ratio of  $k_1/k_{-1} = K_1$  is close to the spectrophotometrically determined  $K_1$  (Table II).

In 30% Me<sub>2</sub>SO the rate of decomposition is very fast for our technique; thus we could not measure the dependence of the rate on hydroxide concentration, and we could only measure  $k_{-1}$ .

In 40% Me<sub>2</sub>SO the observed pseudo-first-order rate constant first decreased with OH<sup>-</sup> concentration and then increased at concentrations higher than 0.2 M (Table IV). Similar behavior was found in reactions of several activated aromatic substrates and methoxide ion in methanol,<sup>14-16</sup>

(10) (a) V. Gold and C. H. Rochester, *J. Chem. Soc. B*, 1727 (1964); (b) E. Buncel, A. R. Norris, K. E. Russell, and P. J. Sheridan, *Can. J. Chem.*, **52**, 25 (1974).

(11) M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967).

(12) (a) F. Terrier, F. Millot, and W. P. Norris, *J. Am. Chem. Soc.*, **98**, 5883 (1976); (b) M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 343 (1978).

(13) C. D. Ritchie, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, 1969, p 221.

(14) M. R. Crampton and H. A. Khan, *J. Chem. Soc., Perkin Trans. 2*, 1173 (1972).

and it was interpreted in terms of ion-pair formation between the complex and the cation.

Our results were obtained at constant ionic strength ( $\mu = 1$  M) by using KCl as the compensating electrolyte, such that the concentration of the cation ( $K^+$ ) was constant, and ion-pair formation cannot explain our results.

We considered the possibility of formation of the 1:2 addition complex 6 according to eq 5. The observed rate constant would be given by eq 10 if we assume faster

$$k_{\text{obsd}} = k_1[\text{OH}^-] + \frac{k_{-1}}{1 + K_5[\text{OH}^-]} \quad (10)$$

equilibration between 2 and 3 than between 3 and 6 or by eq 11 if 3 is a steady-state intermediate.<sup>17</sup> Equation 11

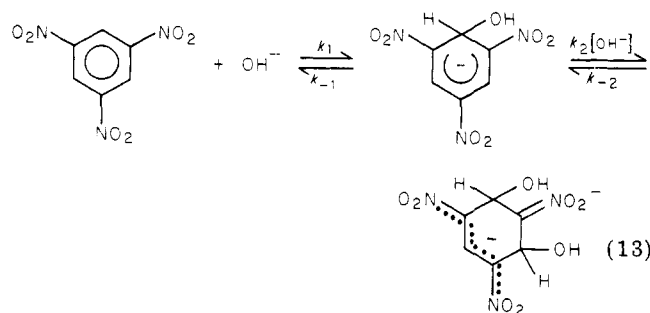
$$k_{\text{obsd}} = \frac{k_1 k_5 [\text{OH}^-]^2}{k_{-1} + k_5 [\text{OH}^-]} + \frac{k_{-1} k_{-5}}{k_{-1} + k_5 [\text{OH}^-]} \quad (11)$$

simplifies to eq 12 if  $k_5[\text{OH}^-] > k_{-1}$ . Both eq 10 and eq

$$k_{\text{obsd}} = k_1[\text{OH}^-] + k_{-1}/K_5[\text{OH}^-] \quad (12)$$

12 predict the observed dependence of  $k_{\text{obsd}}$  on hydroxide concentration.

There are no data in the literature about the kinetics of formation of 1:2  $\sigma$  complexes with substrates bearing an amine substituent, but all of what is known about this type of complex indicates that they form much more slowly than 1:1  $\sigma$  complexes.<sup>18</sup> For instance, for the reaction shown in eq 13,  $k_1 = 33.9 \text{ s}^{-1}$ ,  $k_{-1} = 8 \text{ s}^{-1}$ ,  $k_2 = 5.7 \times 10^{-2}$



$\text{M}^{-1} \text{ s}^{-1}$ , and  $k_{-2} = 6.8 \times 10^{-2} \text{ s}^{-1}$ .<sup>17</sup> It seems very unlikely that formation of complex 6 is faster than formation of 3, and this possibility must be rejected.

As we point out above we believe that complex 3 is deprotonated under these reaction conditions as in eq 6. Since deprotonation of 3 by hydroxide is expected to be a very fast reaction,<sup>19</sup> eq 10 gives the expression for the observed rate if we replace  $K_5$  by  $K_6$ . Equation 10 can be rearranged as in eq 14.

$$\frac{k_{\text{obsd}}}{[\text{OH}^-]} = k_1 + \frac{k_{-1}}{(1 + K_6[\text{OH}^-])[\text{OH}^-]} \quad (14)$$

The plot of the left-hand side of eq 14 vs.  $[\text{OH}^-]^{-2}$  should yield  $k_1$  as intercept. On the other hand,  $k_{-1}$  can be obtained from the plot of  $k_{\text{obsd}}$  vs.  $[\text{OH}^-]$  by extrapolation to zero  $\text{OH}^-$  concentration. This value is in excellent agreement with the value of  $k_{-1}$  determined in the solvent in

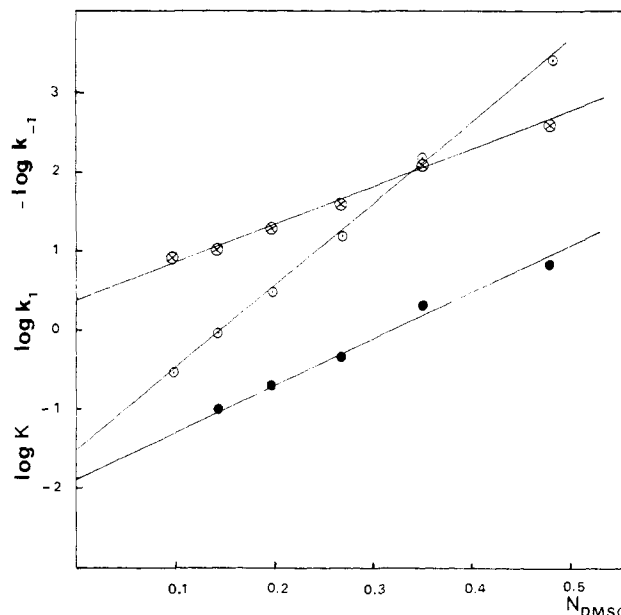
(15) A. Spinelli, G. Consiglio, and R. Noto, *J. Chem. Res. (S)*, 242 (1978).

(16) C. F. Bernasconi, *J. Am. Chem. Soc.*, **90**, 4982 (1968).

(17) C. F. Bernasconi, "Relaxation Kinetics", Academic Press, New York, 1976, Chapter 3.

(18) Buncell reported that the addition of the second molecule of sulfite to diethylpicramide is a much slower process than the addition of the first.<sup>10b</sup>

(19) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).



**Figure 2.** Plots of equilibrium constants ( $\odot$ ), rate constants of formation ( $\bullet$ ), and rate constants of decomposition ( $\otimes$ ) of 3 against mole fraction of  $\text{Me}_2\text{SO}$ .

the absence of KOH (Table II).

Using  $k_1$  and  $k_{-1}$  thus calculated, we rearrange eq 10 and calculate  $K_6$  for each value of  $k_{\text{obsd}}$ . The average of these numbers is  $4.1 \pm 0.2$ , which seems a reasonable value compared with previously determined ionization constants of related compounds.<sup>12b</sup>

The kinetic equilibrium constant  $K_1 = k_1/k_{-1}$  is very close to the value expected from the dependence of  $\log K_1$  vs. mole fraction of  $\text{Me}_2\text{SO}$ , indicating the reliability of our analysis.

We can now go back to eq 7 and calculate the expected values for the optical density by using the  $\epsilon_3$  determined in 60%  $\text{Me}_2\text{SO}$ . We did this, but we did not get a good fit between observed and calculated values. Values of  $K_1$  which are about 3 times smaller are required for a reasonable fit. There are several possibilities that might account for this discrepancy: (1) we are using concentration instead of an acidity function which is probably more adequate at this high concentration of hydroxide; (2) the extinction coefficients of 3 and 7 are not the same as those assumed in eq 7; (3) the operation of a differential salt effect between KOH and KCl. The kinetic equilibrium constant is based on data treated according to eq 10, whereas the spectrophotometric constants are calculated from data via eq 7. Since these two equations are of quite different forms,  $k_{\text{obsd}}$  and  $A$  are expected to respond differently to a differential salt effect, and  $K_1$  and  $K_6$  determined for the two methods should be different.

On the other hand, there is close agreement between kinetic and spectrophotometric  $K_1$  values for solvents of higher  $\text{Me}_2\text{SO}$  content, despite the fact that the ionic strength was not constant. But due to the higher stability of the complex, lower concentrations of  $\text{OH}^-$  were used, and thus all possible salt effects are less important.

**Solvent Effects.** Table II summarizes all the kinetic and equilibrium parameters. Enrichment of the solvent in  $\text{Me}_2\text{SO}$  from 30 to 80% increases  $K_1$   $10^5$ -fold. This increase in  $K_1$  is due both to an increase in  $k_1$  and to a decrease in  $k_{-1}$ . An increase in the activity of the hydroxide ion by desolvation in conjunction with stabilization of the polarizable complex and of the transition state by the polarizable  $\text{Me}_2\text{SO}$  is commonly invoked to rationalize these effects.<sup>5e,20</sup> The plot of  $\log k_1$ ,  $\log k_{-1}$ , and  $\log K_1$

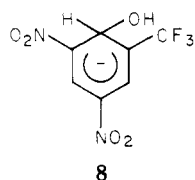
Table V. Kinetic and Equilibrium Parameters for Complexes 3 and 8 in Dimethyl Sulfoxide-Water Mixtures

	8 <sup>a</sup>	3 <sup>b</sup>
	Water <sup>c</sup>	
$10^2 k_1, M^{-1} s^{-1}$	15.9	1.53
$k_{-1}, s^{-1}$	80.6	0.368
$10^3 K, M^{-1}$	2.0	31.1
	60% Me <sub>2</sub> SO	
$k_1, M^{-1} s^{-1}$	24.6	0.458
$10^2 k_{-1}, s^{-1}$	46	2.62
$K, M^{-1}$	53.5	17.5
	70% Me <sub>2</sub> SO	
$k_1, M^{-1} s^{-1}$	126	1.99
$10^2 k_{-1}, s^{-1}$	8.6	0.78
$K, M^{-1}$	1460	254

<sup>a</sup> F. Millot and F. Terrier, *Bull. Soc. Chim. Fr.*, 9, 1823 (1974) (at 20 °C). <sup>b</sup> This work. <sup>c</sup> Values extrapolated.

as a function of mole fraction of Me<sub>2</sub>SO (Figure 2) is a straight line, as seems to be a common finding in Meisenheimer chemistry.<sup>21</sup>

In Table V we compare rate and equilibrium parameters for 3 and 8.



We note that in water solution 3 is more stable than 8,  $K_1(3)/K_1(8) = 15.6$ , and the higher stability of 3 is more the result of slower rate of decomposition than of faster rate of formation. The equilibrium constant for the 1:1 sulfite ion complex of trinitrobenzene is  $2.83 \times 10^{-2} M^{-1}$ ,<sup>22</sup> whereas that of dimethylpicramide is  $3 \times 10^4$ <sup>10b</sup> at 25 °C, and again, the backward reactions are responsible for the

(20) (a) J. W. Larsen, K. Amin, and J. H. Fendler, *J. Am. Chem. Soc.*, 93, 2910 (1971); (b) J. H. Fendler and J. W. Larsen, *J. Org. Chem.*, 37, 2608 (1972).

(21) F. Terrier, F. Millot, and J. Morelli, *J. Org. Chem.*, 41, 3892 (1976).

(22) C. F. Bernasconi and R. Bergstrom, *J. Am. Chem. Soc.*, 95, 3603 (1973).

differences in the equilibrium constants. After the stabilities of complexes with different X substituents<sup>10b</sup> at C-1 were compared, it was suggested that the effect of X on the stability of complexes is mainly due to its effect on solvation of the complex rather than its electronic nature. The much smaller rate constant for the decomposition of 3 with respect to that for 8 may be the result of better solvation of complex 3 by water through hydrogen bonding to the amine group. As Me<sub>2</sub>SO replaces water in the solvent, the stabilization of 3 relative to 8 decreases since less water is available to hydrogen bond to the amine group in the complex, and consequently the ratio  $k_{-1}(3)/k_{-1}(8)$  decreases.

### Experimental Section

Trifluralin (2) was obtained from a commercial sample of Treflan (Eli Lilly) and purified by recrystallization from ethanol; mp 46-47 °C (lit. mp 46-47 °C).<sup>23</sup>

Me<sub>2</sub>SO was dried on 5A-type molecular sieves and vacuum distilled. Solvent mixtures were made up from the desired number of volumes of Me<sub>2</sub>SO in 100 volumes of solution. The mole fraction of Me<sub>2</sub>SO was determined by weighing the Me<sub>2</sub>SO and the final solution.

<sup>1</sup>H NMR studies were carried out on a Varian T 60 spectrophotometer at the probe temperature, and the absorption is reported in  $\delta$  values, relative to Me<sub>4</sub>Si.

Absorbance measurements were obtained by using a Beckman 24 spectrophotometer.

Kinetic measurements were made by rapidly injecting about 10  $\mu$ L of complex 3 prepared in 80% Me<sub>2</sub>SO into the thermostated cell of the spectrophotometer and recording the decrease in absorbance at 430 nm. The temperature inside the cell was maintained at  $25 \pm 0.5$  °C. In solutions where the amount of 3 formed was considerable, we measured the attainment of equilibrium for the formation of 3, starting from a solution of 2. Both methods give the same results. Changes in the wavelength of measurements did not change the observed rate.

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**Registry No.** 2, 3765-92-2; 3, 72283-22-8; potassium hydroxide, 1310-58-3.

(23) "The Merck Index", Paul G. Stecker, Ed., Merck & Co., New York, 1968, p 1074.

## Kinetics and Activation Parameters for the Reduction of Alkylcyclohexanones by Lithium Tri-*tert*-butoxyaluminumhydride<sup>1</sup>

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The kinetics of reduction of 15 cyclohexanones by lithium tri-*tert*-butoxyaluminumhydride in tetrahydrofuran solvent are reported. The data confirm that the reaction is well represented by a simple second-order kinetic process. Second-order rate constants determined at various temperatures are recorded and the activation parameters determined. Rate constants vary from  $5.0 \times 10^{-3}$  to  $4.4 L mol^{-1} s^{-1}$ ; these rate constants exceed those of reduction by NaBH<sub>4</sub> by factors varying from 50 (unhindered cyclohexanones) to 450 (hindered cyclohexanones). The reductions appear to be nearly isoenthalpic, all but three of the values of  $\Delta H^\ddagger$  being in the range  $6.8 \pm 0.8$  kcal mol<sup>-1</sup>. Variations in rates between ketones are caused by changes in  $\Delta S^\ddagger$ , and entropy is also more significant than enthalpy in the free-energy barrier to reaction. Mechanistic aspects of the reduction are discussed.

Despite the intensive use of complex metal hydrides as versatile and stereoselective reducing agents in synthetic

organic chemistry over the past three decades, the parallel development of rigorous mechanistic information on these