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## Carbanions. Electron Transfer vs. Proton Capture. 5. Reaction of 9-Methoxyfluorene with Aromatic Nitro Compounds Catalyzed by Alkali Metal and Tetraalkylammonium Methoxides

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**Abstract:** 9-Methoxyfluorene ion exists in dynamic equilibrium with 9-methoxyfluorene and methoxide ion at 30 °C in methanol. Although the concentration of this carbanion remains small and its reprotonation by methanol is rapid, it can be trapped through one-electron oxidation when aromatic nitro compounds are added to the reaction mixture. Acceptors having sufficiently high reduction potentials, 1,3-dinitrobenzene, 4-cyanonitrobenzene, and 3,5-dichloronitrobenzene, trap most of the carbanions produced, resulting in an ionization-limited formation of oxidation products. Nitrobenzene is a relatively inefficient electron acceptor and reacts reversibly with the carbanion as evidenced by a synergistic improvement in trapping efficiency for the system: nitrobenzene–molecular oxygen. The ionization rate of the carbon acid, the trapping efficiency of nitrobenzene, and the degree to which the electron transfer is reversible are all influenced by the nature and the concentration of the base employed. The second-order rate constant for ionization increases with increasing methoxide concentration for all of the counterions studied. At any particular  $[\text{M}^+\text{OMe}]$  the second-order rate constants are in the order:  $\text{Me}_4\text{NOMe} > \text{KOMe} > \text{NaOMe} > \text{LiOMe}$ . The same order is observed in the nitrobenzene trapping efficiency when the trapping is irreversible (oxygen present). With nitrobenzene alone, however, the electron transfer is highly reversible for the  $\text{Me}_4\text{NOMe}$  reaction and, in the absence of oxygen, the trapping efficiency with  $\text{KOMe} > \text{Me}_4\text{NOMe} \approx \text{LiOMe}$ .

The papers of this series describe our efforts to relate the environment of carbanions to the efficiency of their electron transfer reactions. The medium chosen for most of our previous work had been *tert*-butyl alcohol, a protic but nonpolar solvent in which carbanions are believed to exist as contact ion pairs. We had found<sup>1</sup> that the type of ion pairing dramatically affects the electron transfer efficiency.

By contrast with *tert*-butyl alcohol, the environment of carbanions in polar protic solvents is enigmatic. In methanol, for example, rates and equilibria of carbanion reactions are cation dependent<sup>2</sup> but the usual spectroscopic<sup>3</sup> and stereochemical<sup>4</sup> tests for ion pairing give somewhat ambiguous re-

sults. We therefore decided to study the electron transfer efficiency of a carbanion in this medium as a function of the nature and concentration of its counterion. Of the various systems described in the preceding paper,<sup>5</sup> we selected 9-methoxyfluorene ion for detailed investigation because the products of its reaction with aromatic nitro compounds were most unequivocally the result of one-electron transfer.

### Results and Discussion

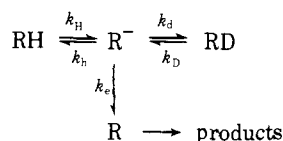
The reaction of carbon acids with alkoxide bases and aromatic nitro compounds has been discussed previously<sup>1,2f</sup> and is related to the present study in Scheme I, where  $k_e = k_e'$

**Table I.** Methoxide-Catalyzed Hydrogen-Deuterium Exchange of I in Methanol-*O-d* at 30 °C

M <sup>+</sup>	[M <sup>+</sup> -OMe]	$k_{H(MeOD)}' \times 10^4,$ M <sup>-1</sup> s <sup>-1</sup>
Li <sup>+</sup>	0.28	3.65
	0.52	4.42
	0.57	4.47
	1.03	5.77
	1.14	6.37
Na <sup>+</sup>	0.26	4.12 <sup>a</sup>
	0.51	5.17
	1.03	6.89
K <sup>+</sup>	0.16	3.76
	0.47	6.03 <sup>b</sup>
	0.93	10.9
	1.31	16.4
	1.53	21.1
	2.03	43.5
	2.29	57.5
	2.62	70.0
	Me <sub>4</sub> N <sup>+</sup>	0.11
	0.26	7.98
	0.32	9.25
	0.53	13.1
	0.64	16.1

<sup>a</sup> Two separate runs gave  $4.04 \times 10^{-4}$  and  $4.20 \times 10^{-4}$  M<sup>-1</sup> s<sup>-1</sup>.<sup>b</sup> Three separate runs gave  $5.97 \times 10^{-4}$ ,  $6.07 \times 10^{-4}$ , and  $6.04 \times 10^{-4}$  M<sup>-1</sup> s<sup>-1</sup>.**Table II.** Rate Constants for the Loss of I in 0.537 N Potassium Methoxide in Methanol-*O-h* at 30 °C under Nitrogen

[I]	[PhNO <sub>2</sub> ]	$k_{\text{loss}} \times 10^5,$ s <sup>-1</sup>	$k_3 \times 10^5,$ M <sup>-2</sup> s <sup>-1</sup>
0.0492	0.115	0.389	6.30
0.0754	0.221	0.732	6.17
0.0508	0.334	1.150	6.41

<sup>a</sup> Pseudo-first-order rate constant for loss of I by gas chromatography vs. internal hexadecane. <sup>b</sup> Third-order rate constant,  $k_3 = k_{\text{loss}}/[\text{PhNO}_2][\text{MeO}^-]$ .**Scheme I**[ArNO<sub>2</sub>],  $k_H = k_H' [\text{MeO}^-]$ ,  $k_h = k_h' [\text{MeOH}]$ , and  $k_d = k_d' [\text{MeOD}]$ .

**Hydrogen-Deuterium Exchange of 9-Methoxyfluorene (I) in Methanol-*O-d*.** When  $[\text{MeOH}] \cong 0$  and  $[\text{ArNO}_2] = 0$ , determination of  $k_H$  is straightforward, being simply the rate constant for deuterium incorporation in I. This exchange reaction was studied as a function of  $[\text{M}^+-\text{OMe}]$  for M = Li, Na, K, and Me<sub>4</sub>N. The results are listed in Table I and plotted in Figure 1. The trends are normal<sup>2</sup> for the alkali metal methoxides and are seen to extend to Me<sub>4</sub>NOMe.

**Methoxide-Catalyzed Reaction of I with Aromatic Nitro Compounds.** When the disappearance of I in the presence of methoxide ion in methanol was followed gas chromatographically, good pseudo-first-order kinetic plots were obtained provided that at least a twofold molar excess of nitroaromatic to I was maintained. The reaction also proved to be first order in nitrobenzene as seen in Table II.

**Table III.** Rate Constants for Loss of 0.05 M I in 0.646 N Potassium Methoxide in Methanol at 30 °C under Nitrogen with Various Substituted Nitrobenzenes Present

Substituent	[Acceptor]	$k_{\text{loss}} \times 10^5,$ s <sup>-1</sup>	$E^{\circ}$ vs. SCE in DMF <sup>a</sup>	V vs. Hg pool in HOAc <sup>b</sup>
None	0.217	1.19	-1.13 <sup>c</sup>	-0.675
4-Cl	0.222	8.34	-1.04 <sup>c</sup>	-0.615
4-C≡N	0.100	18.6	-0.83 <sup>c</sup>	
3,5-Cl <sub>2</sub>	0.105	19.3		-0.490
3-NO <sub>2</sub>	0.138	20.1	-0.82 <sup>d</sup>	-0.560

<sup>a</sup> Contained 0.1 M R<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. <sup>b</sup> Contained 0.1 M NH<sub>4</sub><sup>+</sup>OAc<sup>-</sup>. The reduction potential in this medium may not reflect the stability of ArNO<sub>2</sub><sup>-</sup> but it was the only value that was available for 3,5-dichloronitrobenzene. I. Bergman and J. C. James, *Trans. Faraday Soc.*, **48**, 956 (1952). <sup>c</sup> J. M. Frisch, T. P. Layoff, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 1724 (1965). <sup>d</sup> An average of values taken from C. K. Mann and K. K. Barnes, "Electrochemical Data in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, p 354.

**Table IV.** Effect of the Concentration of 3,5-Dichloronitrobenzene on the Rate of Loss of I (0.05 M) in 0.646 N Potassium Methoxide in Methanol-*O-h* at 30 °C in a Nitrogen Atmosphere

[3,5-Cl <sub>2</sub> PhNO <sub>2</sub> ]	$k_{\text{loss}} \times 10^4,$ s <sup>-1</sup>
0.228	1.93
0.226	2.08 <sup>a</sup>
0.137	1.87 <sup>a</sup>
0.125	1.93
0.105	1.93
0.0094	0.94 <sup>a</sup>

<sup>a</sup> The reactions were run in an oxygen atmosphere.**Table V.** Effect of the Concentration of 1,3-Dinitrobenzene on the Rate of Loss of I (0.05 M) in 0.620 N Potassium Methoxide in Methanol-*O-h* at 30 °C in a Nitrogen Atmosphere

[1,3-(NO <sub>2</sub> ) <sub>2</sub> Ph]	$k_{\text{loss}} \times 10^4,$ s <sup>-1</sup>
0.138	2.02 <sup>a</sup>
0.076	1.95
0.055	1.87
0.036	1.68

<sup>a</sup> This run was carried out with  $[\text{KOMe}] = 0.642$  N.

A number of substituted aromatic nitro compounds were also tried as acceptors in this reaction with the results listed in Table III. A few compounds with more positive half-wave potentials were tried, but they reacted directly with the base under these conditions. The last three entries of Table III show very similar rates and represent ionization limited reaction ( $k_{\text{loss}} = k_H$ ) as demonstrated by their insensitivity to acceptor concentration (Tables IV and V). It was also found that values of  $k_H$  determined from deuterium exchange were very close to  $k_{\text{loss}}$  with 0.2 M 3,5-dichloronitrobenzene present. (See Table VI.) Only in the case of tetramethylammonium ion was a significant discrepancy observed, possibly indicating some internal return in this case. As expected, no deuterium was incorporated in unreacted I after partial consumption by electron transfer to 3,5-dichloronitrobenzene.

It is important to note that the aromatic nitro compounds employed as acceptors do not complex with I prior to ionization. This is suggested by the fact that the ionization rate of I was unaffected by the presence of the acceptor<sup>6</sup> and is proven by its insensitivity to the acceptor:substrate ratio (Table VII).

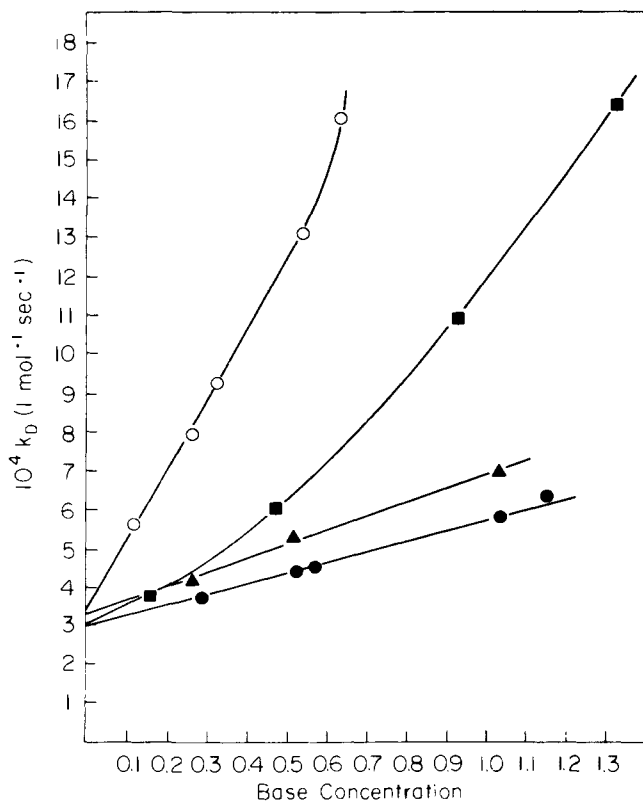


Figure 1. Dependence of second-order rate constant for hydrogen-deuterium exchange on [MOME]. O, M = Me<sub>4</sub>N; ■, M = K; ▲, M = Na; ●, M = Li.

Table VI. Comparison of Rate of Hydrogen-Deuterium Exchange of I with the Rate of Loss of I in the Presence of 0.2 M 3,5-Dichloronitrobenzene at 30 °C in Methanol-*O-d*

M	[MOCH <sub>3</sub> ]	$k_2(\text{loss}),^a$ M <sup>-1</sup> s <sup>-1</sup>	$k_H'(\text{exchange}),$ M <sup>-1</sup> s <sup>-1</sup>	$k_{\text{loss}}/k_H$
K	0.47	$6.16 \times 10^{-4}{}^b$	$6.03 \times 10^{-4}{}^c$	1.02
K	1.53	$2.26 \times 10^{-3}$	$2.11 \times 10^{-3}$	1.07
K	0.48 <sup>d</sup>	$4.45 \times 10^{-5}{}^d$	$4.40 \times 10^{-5}{}^d$	1.01
Na	0.52	$4.91 \times 10^{-4}$	$5.17 \times 10^{-4}$	0.95
Li	0.57	$4.80 \times 10^{-4}$	$4.47 \times 10^{-4}$	1.07
Me <sub>4</sub> N	0.32	$1.17 \times 10^{-3}$	$9.25 \times 10^{-4}$	1.26

<sup>a</sup>  $k_{\text{loss}}/[\text{MOCH}_3]$ . <sup>b</sup> Average of four runs. <sup>c</sup> Average of three runs. <sup>d</sup> These data were obtained using I-*d* and methanol-*O-h*.

Even the improbable case of an equilibrium-favored 1:1 or 1:2 complex of I to acceptor with an ionization rate identical with I is ruled out by the data of Table VII.

The rate of reaction of I with nitrobenzene, a relatively inefficient acceptor, was then determined as a function of the nature and concentration of the base. These results are listed in Table VIII and compared with ionization rates determined under the same conditions. We were surprised to discover that the rates of the potassium and tetramethylammonium methoxide catalyzed loss of I were increased by the presence of molecular oxygen.

Although the catalysis of base-catalyzed hydrocarbon autoxidation by aromatic nitro compounds is a well-documented phenomenon,<sup>7</sup> the reverse effect, catalysis of reaction with the nitro compound by oxygen, has been overlooked in previous work. Oxygen, by itself, reacts much more slowly with I than nitrobenzene does,<sup>8</sup> making the combined effect synergistic.

This interesting synergistic effect of nitrobenzene and oxygen indicates that the reaction between nitrobenzene and

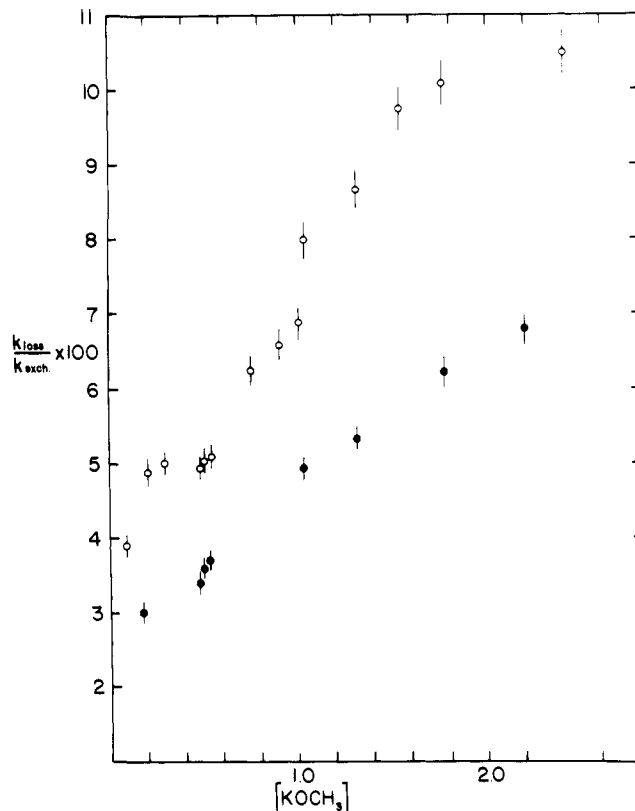


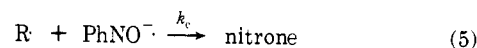
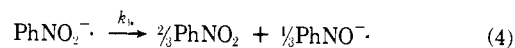
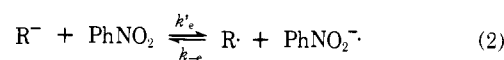
Figure 2. Dependence of nitrobenzene trapping efficiency on [KOME] in the presence and absence of oxygen. O, O<sub>2</sub> present; ●, O<sub>2</sub> absent.

Table VII. The Effect of Variations in the Ratio of I to 3,5-Dichloronitrobenzene on the Rate of Loss of I in Methanol-*O-d* Catalyzed by 0.47 N Potassium Methoxide at 30 °C

[I]	[ArNO <sub>2</sub> ]	[I]/[ArNO <sub>2</sub> ]	$k_2(\text{loss}) \times 10^4, \text{M}^{-1} \text{s}^{-1}$
0.203	0.101	2	5.9
0.100	0.101	1	6.2
0.0507	0.102	0.5	6.1
0.0772	0.0261	3	6.4 <sup>a</sup>

<sup>a</sup> Approximate value from initial slope of rate plot.

#### Scheme II



9-methoxyfluorene is reversible under anaerobic conditions. Oxygen is known to react rapidly with nitrobenzenide ion<sup>9</sup> and the 9-methoxyfluorenyl radical is also intercepted by oxygen as evidenced by a change in reaction products.<sup>5</sup>

The reaction was shown to be irreversible in the presence of oxygen by demonstrating that the rate of loss of I was unaffected by changes in the partial pressure of oxygen over the solution (Table IX). As the concentration of oxygen in solution is directly related to its partial pressure, it is evident that the

**Table VIII.** Rate Constants and Apparent Carbanion Trapping Efficiency in the Reaction of Ia-*d*<sup>a</sup> with Lithium, Sodium, Potassium, and Tetramethylammonium Methoxide and 0.2 M Nitrobenzene under Oxygen and under Nitrogen at 30 °C in Methanol-*O-d*

M	[MOCH <sub>3</sub> ]	$k_2(\text{loss}) \times 10^5,^b$ M <sup>-1</sup> s <sup>-1</sup> , under N <sub>2</sub>	$(k_{\text{loss}}/k_{\text{H}}) \times 100^c$ under N <sub>2</sub>	$k_2(\text{loss}) \times 10^5,^b$ M <sup>-1</sup> s <sup>-1</sup> , under O <sub>2</sub>	$(k_{\text{loss}}/k_{\text{H}}) \times 100^c$ under O <sub>2</sub>
(CH <sub>3</sub> ) <sub>4</sub> N	0.050	0.88	2.1		
	0.056			1.37	2.9
	0.104			1.85	3.3
	0.179			3.13	4.7
	0.26	1.71	2.1		
	0.321			5.03	5.4
	0.46			9.65	8.2
	0.53	2.85	2.1		
	0.64	3.27	2.0	17.1	10.6
	0.18			0.67	2.0
Li	0.28	0.62	1.6		
	0.57	0.64	1.4	0.79	1.8
	1.03	0.86	1.5		
	1.14	0.87	1.4	0.92	1.5
	1.03	2.87	4.1		
Na	0.26	1.06	2.6		
	0.51	1.58	3.1		
	1.03	2.87	4.1		
K	0.094			1.17	3.9
	0.16	1.16	3.0		
	0.200			1.95	4.9
	0.292			2.39	5.1
	0.48	2.10	3.4	3.12	5.0
	0.50	2.26 ± 0.14 <sup>d</sup>	3.6	3.30 ± 0.13 <sup>d</sup>	5.0
	0.53	2.43	3.7		
	0.54			3.51	5.1
	0.78			5.76	6.3
	0.90			7.0	6.6
	1.00			8.1	6.9
	1.07	6.24	5.0	10.1	8.0
	1.31	8.78	5.4	14.2	8.7
	1.76	19.4	6.2	31.4	10.1
	2.20	36.5	6.8	56.1	10.5

<sup>a</sup> 9-Methoxyfluorene was deuterated in the 9 position. Its concentration was 0.05 M for most runs. <sup>b</sup> The first-order rate constant for disappearance of Ia was determined by gas chromatography vs. internal hexadecane and divided by the base concentration. <sup>c</sup> The actual fraction of carbanions trapped by reaction with nitrobenzene may be obtained by multiplying each value by a factor of 5.5 which is the primary isotope effect on ionization. Rate constants for exchange were interpolated from the data of Table I. <sup>d</sup> This is mean value of four separate runs. The error limit represents one standard deviation.

intermediate which is reversibly formed under nitrogen is completely trapped by oxygen.

**Interpretation of Kinetic Data.** A complete sequence of the reactions believed to occur when I-*d* is treated with nitrobenzene in methanol-*O-d* containing alkali metal or tetramethylammonium methoxides is given in Scheme II. Steps 3 and 4 are reasonably assumed to be irreversible based on the apparent stability of the dimer and the relative reduction potentials of nitrobenzene and nitrosobenzene.<sup>10</sup>

If the steady state assumption is made for R<sup>-</sup>, R<sup>•</sup>, PhNO<sub>2</sub><sup>-•</sup>, and PhNO<sup>-•</sup>, the apparent first-order rate constant for loss of 9-methoxyfluorene,  $k_{\text{loss}}$ , is related to the rate constants for the intermediate steps by eq 6, where  $x$  is the kinetic order of

$$k_{\text{los}} = \frac{k_{\text{D}}k_{\text{e}}}{\frac{k_{\text{d}}k_{-\text{e}}[\text{PhNO}_2^{-\bullet}]^{(2-x)/x}}{3\sqrt{k_{\text{a}}k_{\text{b}}}} + k_{\text{d}} + k_{\text{e}}} \quad (6)$$

mechanistic step 4. Even under anaerobic conditions where step 2 is reversible, the reaction kinetics were pseudo first order, strongly suggesting that step 4 is second order ( $x = 2$ ). This is supported by an existing kinetic study of the destruction of the nitrobenzoate radical dianion in aqueous solution.<sup>11</sup>

In the presence of oxygen, step 2 should become irreversible and eq 6 collapses to eq 7. The value of  $k_{\text{D}}$  can be calculated

$$k_{\text{loss}}(\text{O}_2) = \frac{k_{\text{D}}k_{\text{e}}}{k_{\text{d}} + k_{\text{e}}} \quad (7)$$

from the measured values of  $k_{\text{H}}$  and the previously determined isotope effect ( $k_{\text{H}}/5.5 = k_{\text{D}}$ ).<sup>12</sup> By using values of  $k_{\text{D}}$  and  $k_{\text{loss}}$  in the presence and absence of oxygen, rate constant ratios reflecting the partition of both R<sup>-</sup> and R<sup>•</sup> may be calculated. These are listed in Table X for representative base concentrations. Data for the lithium methoxide catalyzed reaction are not given in Table X because  $k_{\text{d}}/k_{\text{e}}$  varies only slightly (9.0–11.1) over the range (0.18–1.14 M), and the reaction is irreversible even with oxygen absent, making it impossible to calculate  $k_{\text{e}}/3\sqrt{k_{\text{a}}k_{\text{b}}}$ . The behavior of sodium methoxide seemed intermediate between that of lithium and potassium methoxide and was not studied in the presence of oxygen.

### Summary and Conclusions

The experimental observations of this study are summarized in the Abstract and are reasonably interpreted in terms of the mechanism of Scheme II. The observed cation dependencies of the various rate constants and their ratios deserve explanation, and we cannot resist the temptation of some brief and possibly premature speculation. The rate constant ratios of Table X can be represented graphically in the free-energy schematic of Figure 4 where the actual free-energy differences are related exponentially to the rate constants. The third transition state is a composite of the transition states of two reactions.

It may be said with certainty that the second transition state is lowered with respect to the first and third with increasing

**Table IX.** Effect of Oxygen Concentration on the Rate of Loss of I-d in the Presence of 0.200 M Nitrobenzene and 0.50 M Potassium Methoxide in Methanol-O-d at 30 °C

% oxygen <sup>a</sup>	$k_2(\text{loss}) \times 10^5,$ $\text{M}^{-1} \text{s}^{-1}$
0	2.26 ± 0.14
5	3.21
20	3.15
100	3.23

<sup>a</sup> Percent by volume of oxygen in the oxygen-nitrogen atmosphere present in the reaction vessel. The total pressure was 1 atm in all cases.

**Table X.** Rate Constant Ratios Reflecting Partition of R<sup>-</sup> and R<sup>•</sup> at Various Methoxide Concentrations

M <sup>+</sup>	[MOMe], M	$k_D \times 10^4,$ $\text{M}^{-1} \text{s}^{-1}$	$k_d/k_e$	$k_{-e}/$ $3\sqrt{k_a k_b}$
Me <sub>4</sub> N	0.056	0.76	4.7	0.93
	0.26	1.45	2.6	1.9
	0.64	2.93	0.71	10.4
K	0.20	0.74	2.8	0.27
	0.50	1.15	2.5	0.21
	1.07	2.34	1.3	0.37
	2.20	9.6	0.70	0.44

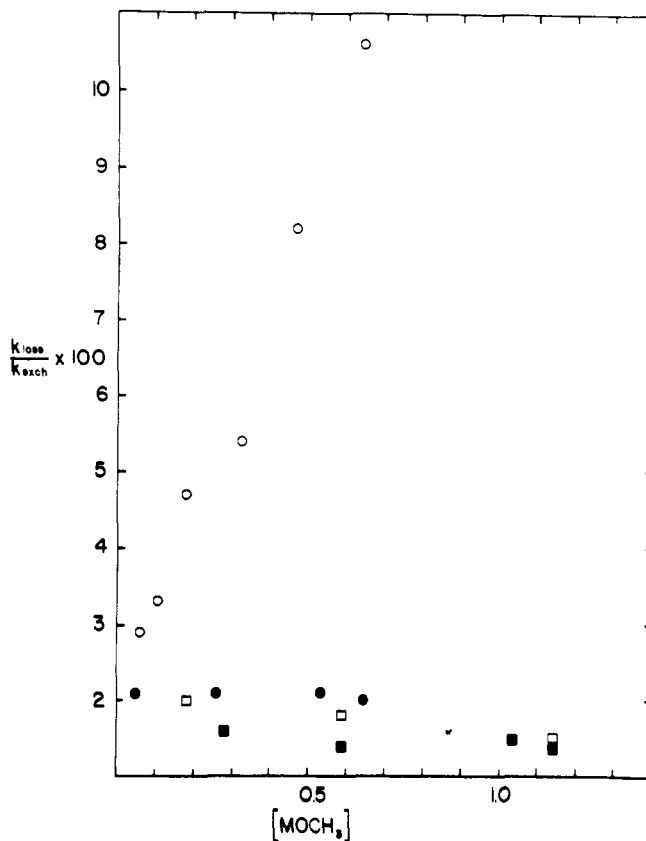
<sup>a</sup> Based on  $k_H/k_D = 5.5$  and interpolation or extrapolation of the data of Table I.

[Me<sub>4</sub>NOMe]. The energy differences correspond to rate factors of 16.5 between the second and third and 6.6 between the first and second for a tenfold increase in [Me<sub>4</sub>NOMe]. With potassium methoxide the second and third transition states maintain a relatively constant relationship, while the first increases relative to the second by a rate factor of four over an 11-fold increase in [KOMe]. Thus the main difference between the two systems is that the electron-transfer step, which is rate controlling for both systems at low base concentrations, increases in rate as [Me<sub>4</sub>NOMe] is increased, making nitrobenzene destruction rate controlling at high concentration. This does not happen with increasing [KOMe] and the nitrobenzene destruction rate has only a minor influence on the overall rate even at [KOMe] = 2.2 M. For lithium methoxide the electron-transfer step is rate controlling throughout the concentration range, and the slight reversibility observed in potassium methoxide disappears.

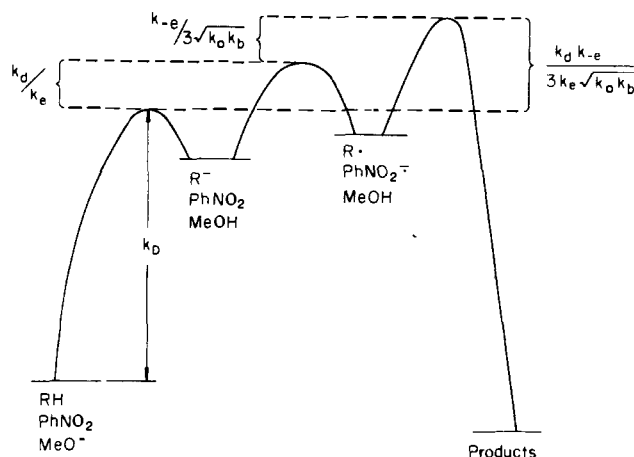
In an attempt to understand these phenomena, we have recently begun to study the reaction of fluorenone with nitrobenzene in methoxide-methanol. Because of the greater acidity of fluorenone, we can directly measure the rate of conversion of carbanions to products. In terms of Figure 4, we are proceeding from the first intermediate to products. The overall rate constant for disappearance of carbanion is given by eq 8, where the asterisks are affixed to rate constants characteris-

$$k_{\text{loss}}^* = \frac{k_{-e}^* \sqrt{6k_a^* k_b}}{k_{-e}^*} \quad (8)$$

tic of the fluorenone system. Several preliminary results<sup>3c</sup> are important to the interpretation of the behavior of I. First,  $k_{\text{loss}}^*$  is independent of [Me<sub>4</sub>NOMe] and strongly dependent on [KOMe]. Secondly, both fluorenone and nitrobenzene ions show spectral changes assignable to ion pairing when tetramethylammonium methoxide is used as base. The spectral characteristics of the lithium and potassium salts are indistinguishable and concentration independent. Finally the apparent  $K_a$  for fluorenone is nearly independent of [Me<sub>4</sub>NOMe]



**Figure 3.** Dependence of nitrobenzene trapping efficiency on [MOMe] in the presence and absence of oxygen. O, M = Me<sub>4</sub>N, O<sub>2</sub> present; ●, M = Me<sub>4</sub>N, O<sub>2</sub> absent; □, M = Li, O<sub>2</sub> present; ■, M = Li, O<sub>2</sub> absent.



**Figure 4.** Rate constants and rate constant ratios responsible for free-energy changes in the reaction of 9-methoxyfluorenone with methoxide and nitrobenzene.

but dramatically increases with increasing [KOMe].

If it may be assumed that 9-methoxyfluorenone and fluorenone ions would be similarly affected by the nature and concentration of the various cations, some tentative interpretations are possible. The most unavoidable of these is that the rate constant for electron transfer between carbanion and nitrobenzene increases with increasing [Me<sub>4</sub>NOMe]. The behavior of  $k_{\text{loss}}^*$  indicates that the energy separation of R<sup>-</sup> and the transition state for product formation (third transition state in Figure 4) is independent of [Me<sub>4</sub>NOMe], yet the separation of the second and third transition states increases. This influence of cation concentration is unexpected for the interconversion of two ion pairs if cation and electron are transferred together. Ion pair dissociation schemes predict either no effect

or a rate retardation. It therefore seems possible that two cations are involved. If nitrobenzene complexed to the carbanion on the face opposite to the tetramethylammonium ion, dissociation could await the arrival of another counterion. This explanation is undoubtedly oversimplified, because the rate increase is greater than the concentration increase.

It seems very unlikely that  $[\text{Me}_4\text{NOMe}]$  would have any effect on the equilibrium constant  $k_e/k_{-e}$  and if this is assumed, it may be calculated that  $k_d$  increases by a factor of 2.5 as  $[\text{Me}_4\text{NOMe}]$  is increased tenfold. Table X shows that  $k_{D'}$  increases by a factor of 3.9 so that  $K_a = k_{D'}/k_d$  would increase by only 1.5. This line of reasoning is supported by the observed invariance of  $K_a$  for fluoradene under these conditions. That the equilibrium in which  $\text{R}^-\text{M}^+$  is produced from presumably free  $\text{MeO}^-$  would not be affected by  $[\text{M}^+]$  might at first seem peculiar, but this is possible provided that the equilibrium,  $\text{R}^- + \text{M}^+ \rightleftharpoons \text{R}^-\text{M}^+$ , lies entirely to the right throughout the concentration range studied. For fluoradene, the value of  $K_a$ , while independent of  $[\text{Me}_4\text{NOMe}]$ , remains greater than  $K_a$  in potassium methoxide at all concentrations. Presumably  $K_a$  would become dependent on  $[\text{Me}_4\text{NOMe}]$  at some low concentration where an appreciable fraction of free  $\text{R}^-$  was present.

The nature of the carbanion and nitrobenzenide ion in potassium methoxide is less certain. It seems clear that they are "less ion paired" in the sense that if ion pairs are present, they are solvated to the extent that the spectral properties of the anion do not reflect the character of the cation. Nevertheless, both ionization rates and  $K_a$ 's for carbon acids increase with increasing  $[\text{KOME}]$  as demonstrated by the observations above and those of other workers.<sup>2</sup> This might be viewed as a gradual approach to ion pairing possibly due to desolvation of potassium ions with increasing concentration. Whatever the reason, the effect seems to be the stabilization of delocalized anions. Thus, we would expect the energies of  $\text{R}^-$  and  $\text{PhNO}_2^-$  to be lowered relative to  $\text{CH}_3\text{O}^-$ . The decomposition of  $\text{PhNO}_2^-$  probably involves disproportionation to a dianion which also has more delocalization of charge than  $\text{CH}_3\text{O}^-$ . One might then predict that, in reference to Figure 4, the second and third transition states, inasmuch as they connect two delocalized anions, should be lowered in energy relative to the first by increasing  $[\text{KOME}]$ . Actually, because  $k_b$  appears in the rate expression as its square root, the energy of the third transition state is inherently insensitive to  $[\text{KOME}]$ , which may account for the apparent mild increase in the energy separation of the second and third transition states.

The data obtained for fluoradene suggest that the equilibrium constants  $k^*/k_{-e}$ , and by inference  $k_e/k_{-e}$ , increase with increasing  $[\text{KOME}]$ . This lowering of the energy of nitrobenzenide relative to the carbanions by increasing  $[\text{KOME}]$  is unexpected based on the preceding delocalization argument. It must be remembered, however, that our system is one in which ion pairing and hydrogen bonding are in competition. For methoxide ion, hydrogen bonding is the dominant stabilizing effect, whereas for the carbanions, ion pairing assumes a greater role. In the absence of hydrogen bonding, the ion pairs of charge-localized anions have lower dissociation constants than ion pairs of delocalized anions.<sup>13</sup> If the energy benefit to nitrobenzenide ion resulting from hydrogen bonding is small or if hydrogen bonding and ion pairing can occur cooperatively, then the apparent increase in  $k_e/k_{-e}$  with increasing  $[\text{KOME}]$  would be explained. Actually, although nitrobenzenide is viewed as a localized anion relative to the anion radicals of hydrocarbons,<sup>13</sup> the ion owes its stability to the even distribution of charge on both oxygens. Hydrogen bonding would oppose this effect.

The certainty of our conclusions for the reaction of I is limited by the fact that we can only measure the differences in transition state free energies and not individual rate con-

stants. We hope to measure the cation dependence of  $k_b$  directly, at which time the data of this paper will be reexamined.

## Experimental Section

**9-Methoxyfluorene** was prepared from 9-bromofluorene<sup>14</sup> by a published procedure.<sup>15</sup> The material thus synthesized contained fluorenone as an impurity. This was removed in the following way. Roughly 6 g of impure 9-methoxyfluorene was allowed to dissolve in 50 ml of ethanol containing 0.5 g of sodium acetate, 2 ml of acetic acid, and 1 g of hydroxylamine hydrochloride. The resultant solution was refluxed for 30 min, cooled, and poured into 200 ml of distilled water. The crystals were separated by filtration, washed with 50 ml of distilled water, dried, and sublimed to give pure 9-methoxyfluorene, mp 43.5 °C (lit.<sup>14</sup> 42–43 °C). This material decomposed slowly on standing in air, but was stable if stored in a dry, oxygen-free atmosphere.

**9-Methoxyfluorene-9-d.** This was prepared by carrying out two consecutive treatments of 9-methoxyfluorene with potassium methoxide in methanol-*O-d* under conditions very similar to the kinetic runs described below.

**Aromatic Nitro Compounds.** All of the nitro compounds used were commercially available. Solids were recrystallized and sublimed and liquids were distilled before use. The purification of nitrobenzene has been described previously.<sup>15</sup>

**Solvents and Solutions.** Reagent grade, anhydrous methyl alcohol was purified by distillation from calcium oxide through a 1-m column packed with glass helices. It was stored over type 3A molecular sieves. Methanol-*O-d* was prepared by a published procedure.<sup>16</sup> Solutions of alkali metal methoxides in methanol were prepared by adding the metal to the alcohol under oxygen-free conditions.

Tetramethylammonium methoxide was prepared from tetramethylammonium fluoride and lithium methoxide by a published procedure.<sup>17</sup>

**Kinetic Procedure for Hydrogen-Deuterium Exchange Reaction.** 9-Methoxyfluorene was allowed to dissolve in a measured volume of methanol-*O-d* in a side-arm flask fitted with a septum attachment. The contents of the flask were degassed by the freeze-thaw technique and the flask filled with oxygen-free nitrogen or argon. The flask and its contents were then equilibrated for 30 min at 30 °C and the reaction initiated by injection of the appropriate amount of base solution. Aliquots were removed at regular intervals (usually 2 ml) and quenched in a mixture of 60 ml of pentane and 100 ml of distilled water. The aqueous layer was washed with an additional 30 ml of pentane and the combined organic layers dried over anhydrous sodium sulfate. Removal of the pentane under reduced pressure gave partially deuterated 9-methoxyfluorene, suitable for low-voltage mass spectral analysis without further purification.

**Kinetic Procedure for Electron-Transfer Reactions under Anaerobic Conditions.** The reactions were carried out in the manner described for exchange reactions except that a weighed amount of aromatic nitro compound and an internal standard, usually hexadecane, were placed in the reaction vessel along with the 9-methoxyfluorene. Base solution was injected to start the reaction, and aliquots were withdrawn and put through the workup procedure described for exchange reactions. The residue after removal of pentane was analyzed by gas chromatography on a 15–17 ft  $\times$  1/4 in. column packed with either SE-30 or SF-96 silicone grease (20% on Chromosorb W) at 200 to 250 °C.

**Kinetic Procedure for the Electron-Transfer Reaction in an Oxygen Atmosphere.** The procedure described above for anaerobic reactions was employed except that the reaction flask was attached to a 1000-ml bulb and the entire assembly evacuated and filled with oxygen (passed over silica gel followed by ascarite) prior to addition of solvent. The total volume of reacting solution was 10 ml for most runs. Vigorous magnetic stirring was maintained throughout the course of the reaction. Workup and analysis were the same as for the anaerobic runs.

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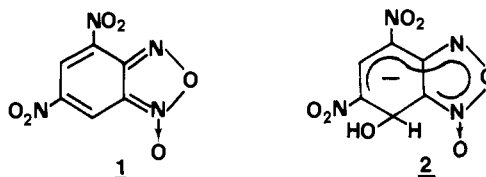
## Meisenheimer Complexes: A Kinetic Study of Water and Hydroxide Ion Attacks on 4,6-Dinitrobenzofuroxan in Aqueous Solution<sup>1</sup>

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**Abstract:** In aqueous solution, 4,6-dinitrobenzofuroxan (**1**) gives a very stable Meisenheimer-type adduct **2**, which is completely formed at pH 5. The kinetics of formation and decomposition of **2** have been studied by the stopped-flow method between pH 1 and 13. At pH < 7, the formation of **2** appears to arise exclusively from the attack of a water molecule on the substrate **1**, which is apparently the first report of this kind in the field of Meisenheimer complexes. At pH > 7, the hydroxide-ion attack starts to compete with that of water; at pH > 9 the reaction  $\mathbf{1} + \text{OH}^- \rightarrow \mathbf{2}$  is the only one observed. At pH > 10.6, the oscilloscope pictures reveal the existence of a fast equilibrium between **2** and a new species **3**, which is completely formed at pH 13 and identified as the dianion arising from the ionization of the hydroxyl group of the adduct **2**. The thermodynamic and kinetic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  for the various reactions have been determined. The formation and decomposition of **2** are subject to general base and general acid catalysis, respectively. Possible mechanisms for the reactions are discussed on the basis of the buffer catalysis effects and deuterium isotope effects. In particular, the abnormally high values obtained for the rate constants for base catalysis by carbonate and bicarbonate ions suggest a nucleophilic attack of these anions on **1** to give an unstable Meisenheimer-type intermediate.

Recently, nitrobenzofuroxans and benzofurazans have been reported to be potent in vitro inhibitors of nucleic acid synthesis in lymphocytes.<sup>3-5</sup> These antileukemic properties have been tentatively interpreted in terms of an easy Meisenheimer-type adduct formation<sup>6</sup> between the substrates and the essentially cellular SH and/or amino groups. In fact, such an explanation is not unreasonable, since some compounds of the series, such as 4,6-dinitrobenzofuroxan,<sup>7,8</sup> 4-nitrobenzofuroxan,<sup>3</sup> and 4-nitrobenzofurazan<sup>3</sup> are known to react with nucleophiles to give very stable Meisenheimer complexes. It was thus of interest to investigate kinetically the behavior of these compounds towards nucleophiles and, in particular, towards hydroxide and thiolate anions in order to get a better understanding of the reactions. Following a preliminary communication,<sup>9</sup> we report first a comprehensive study of the kinetics of formation and decomposition of the hydroxyl adduct **2** derived from 4,6-dinitrobenzofuroxan (**1**) in aqueous solution. Our results reveal some interesting and new features, which are due to the very strong electron-withdrawing character of the annelated furoxan ring. In particular, the fact that the adduct **2** may be formed from the attack of water on **1** is



apparently the first report of this sort in the field of Meisenheimer complexes.

### Results

In aqueous solution, 4,6-dinitrobenzofuroxan (**1**,  $\lambda_{\text{max}} 415 \text{ nm}$ ,  $\epsilon 7050 \text{ M}^{-1} \text{ cm}^{-1}$ ) has been shown to give rapidly the yellow-colored adduct **2**, which was identified by NMR and visible spectroscopy<sup>7-10</sup> ( $\lambda_{\text{max}} 462.5 \text{ nm}$ ,  $\epsilon 24 400 \text{ M}^{-1} \text{ cm}^{-1}$ ) and which is completely formed at pH 5. To carry out a comprehensive study of the formation and decomposition of **2**, we have therefore investigated these reactions between pH 0.8 and 13, using dilute hydrochloric acid solutions, various buffer solutions, and dilute potassium hydroxide solutions. The ionic strength ( $\mu$ ) was always kept at 0.2 M by adding KCl as nec-