

Intermediates in Nucleophilic Aromatic Substitution. VIII.^{1,2}
Kinetic and Proton Magnetic Resonance Investigations of the
Interaction of Methoxide Ions with 1-Methoxy-2,4,5-trinitronaphthalene

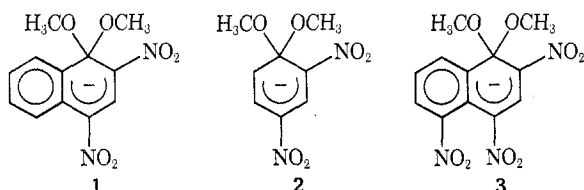
J. H. FENDLER³ AND E. J. FENDLER³

Radiation Research Laboratories, Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

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The rate constants (k_1) for the formation of the methoxyl complex of 1-methoxy-2,4,5-trinitronaphthalene (**3**) in methanol at 13.45, 25.00, and 35.00° have been determined spectroscopically by following the increase in absorbance at 495 nm as a function of time in $3.35 \times 10^{-6} M$ solutions of 1-methoxy-2,4,5-trinitronaphthalene (**5**) in the presence of methoxide ions [$(3.3 - 82.7)10^{-4} M$]. The rate constants (k_2) for the decomposition of **3** have been determined directly at the same three temperatures by following the decrease in the absorbances of dilute methanolic solutions of the isolated complex **3**. From these values the equilibrium constant for the formation of **3** ($K_{25.00^\circ} = 2.93 \times 10^4 \text{ l. mol}^{-1}$) and the enthalpies and entropies of activation both for the formation and decomposition of **3** have been obtained. These data indicate **3** to be more stable than 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylidene ion ($K_{25.00^\circ} = 1.7 \times 10^4 \text{ l. mol}^{-1}$) or the methoxyl complex of 1-methoxy-2,4-dinitronaphthalene ($K_{25.00^\circ} = 230 \text{ l. mol}^{-1}$). The stabilities of these complexes are discussed. The rate of decomposition of crystalline **3** has also been examined in aqueous buffers in the pH range of 5.63–10.96; the decomposition is acid catalyzed. The structure of **3** has been established from pmr spectra of both the isolated and the *in situ* generated complex. A comparative discussion of the pmr parameters is offered.

In a previous part of this series we have reported that the equilibrium constant for the formation of the methoxyl complex of 1-methoxy-2,4-dinitronaphthalene (**1**)⁴ is several orders of magnitude greater than that obtained for the corresponding complex of 2,4-dinitroanisole⁵ (**2**). This result is a reflection of the greater



resonance energy required for the stabilization of structure **2** than that for **1**.⁶

Although studies of nucleophilic aromatic substitution in polyaromatic systems are potentially important, there have been relatively few mechanistic investigations concerning the transmission of electronic effects from one ring to the other in substituted naphthalenes and other polyaromatic systems. Ellias and Parker have found that the rate constant for the reaction of aniline with 1-chloro-2,4,5-trinitronaphthalene is only greater than that with 1-chloro-2,4-dinitrobenzene by a factor of 14 in ethanol at 25.0°, whereas the corresponding difference in reactivity between 2,4-dinitro- and 2,4,6-trinitrochlorobenzene is 16,100.⁷ The effects

of nitro groups in the 2,4,5⁸ and in the 2,4,7⁹ positions of 1-methoxy-substituted naphthalenes on the rates of symmetrical methoxyl exchange reactions have been investigated. The nature of these experiments did not allow, however, quantitative information to be obtained for all of the processes involved.^{8,9} As a part of our systematic studies on the structures and reactivities of Meisenheimer complexes we have determined kinetic and thermodynamic parameters for the formation and decomposition of the methoxyl complex of 1-methoxy-2,4,5-trinitronaphthalene (**3**) in methanol and have obtained proton magnetic resonance parameters both for the isolated and for the *in situ* generated complex **3**.

Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.¹⁰ N,N-Dimethylacetamide, DMA (Baker analyzed reagent grade) was stored over Linde Type 5A molecular sieve and its purity was verified by its pmr spectrum.

1-Chloro-2,4,5-trinitronaphthalene (**4**) was prepared by the method of Rindl.¹¹ After recrystallization from benzene-acetic acid (50:50, v/v) using decolorizing charcoal, **4** melted at 143–144° (lit.¹¹ mp 143–144°).

1-Methoxy-2,4,5-trinitronaphthalene (**5**) was prepared by the dropwise addition of 1.30 ml of 5.05 M (6.54 mmol) potassium methoxide in methanol to a hot solution of **4** in 75 ml of anhydrous methanol. The reaction mixture was refluxed for 30 min, allowed to cool slowly to room temperature, cooled to ~0° with an ice bath, and filtered. The yellow crystals were recrystallized from acetic acid, mp 151.5–152° (lit.¹¹ mp 150.5–151.5°).

The methoxy complex (**3**) of 1-methoxy-2,4,5-trinitronaphthalene was prepared by the addition of 0.421 ml of 5.05 M (2.125 mmol) potassium methoxide in methanol to a solution of 0.6325 g (2.16 mmol) of **5** in 1.5 ml of dry dioxane. After evaporation of some solvent with dry nitrogen and cooling, the red crystals were filtered under nitrogen and washed with dry benzene (three times) and anhydrous ether (twice). Pulverization of the crystals in a dry nitrogen atmosphere and drying *in vacuo* over P₂O₅ gave a red solid, mp 180° dec.

(1) Part VII: E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larsen, *J. Org. Chem.*, **35**, 287 (1970).

(2) For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution, see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncl, A. R. Norris, and K. E. Russell, *Quart. Rev. (London)*, **22**, 123 (1968); (c) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (f) F. Pietra, *Quart. Rev. (London)*, **23**, 504 (1969).

(3) Department of Chemistry, Texas A & M University, College Station, Texas 77843.

(4) J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 977 (1968).

(5) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).

(6) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p 177.

(7) D. H. D. Ellias and R. E. Parker, *J. Chem. Soc.*, 2616 (1962).

(8) N. A. Katsanos, *Z. Phys. Chem. (Frankfurt am Main)*, **63**, 168 (1969).

(9) D. S. Gilbert, Thesis, Leicester College of Technology, Leicester, England, 1963.

(10) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

(11) M. Rindl, *J. Chem. Soc.*, 1911 (1913).

*Anal.*¹² Calcd for C₁₂H₁₀KN₃O₆: C, 39.7; H, 2.76; K, 10.8; N, 11.6. Found: C, 38.3; H, 2.7; K, 10.8; N, 11.0.¹³

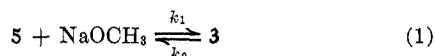
The attainment of the equilibrium for the formation of complex **3** from **5** in methanol was followed at 500 nm in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The temperature was measured inside the cells and was maintained within $\pm 0.02^\circ$. The mixing techniques for fast reactions have been described previously.¹⁵

The rate constants for the decomposition of the solid complex **3** in methanol and in aqueous buffers were obtained by following the rates of decrease in absorbance at 500 nm in appropriate solutions of **3** in the thermostated cell compartment of the spectrophotometer. The pH of the buffer solutions was measured at 25.00° with an Orion-801 digital pH meter. Since the concentration of **5** was kept at least tenfold smaller than that of the sodium methoxide and since the concentration of the complexes were in the order of $5 \times 10^{-6} M$, pseudo-first-order kinetics were observed for both the attainment of the equilibrium for **3** and for the decomposition of complex **3**. Such first-order plots for typical runs are given in Figure 1.

Pmr spectra (60 MHz) were obtained with a Varian Associates A-60 spectrometer at ambient probe temperature (31°) or at 25° (probe temperature maintained with a V6040 variable temperature controller). All spectra were determined on solutions in DMSO-*d*₆ or in DMA using tetramethylsilane (TMS) as an internal standard; chemical shifts are given on the τ scale in ppm relative to TMS ($\tau = 10.00$ ppm) and are accurate to ± 0.03 ppm. Chemical shift data were taken from spectra determined at sweep widths of 500 Hz or were calculated from the average resonance frequencies observed at 50-Hz sweep widths (at least three determinations) using the computer program LAOCOON III.¹⁶ The reported coupling constants were calculated simultaneously with LAOCOON III and are accurate to ± 0.2 Hz.

Results

Upon the addition of sodium methoxide to dilute methanolic solutions of **5** the development of a red color is observed. The intensity of this color above $10^{-1} M$ NaOCH₃ remains constant over a large range of alkoxide ion concentration indicating that the equilibrium (eq 1)



is complete. In the concentration range of $3.3\text{--}82.7 \times 10^{-4} M$ methanolic sodium methoxide and $3.34 \times 10^{-5} M$ **5**, it was possible to follow the attainment of the equilibrium by measuring the increase in absorbance at 495 nm [ϵ_{495} of **3** = $(1.9 \pm 0.1)10^4 \text{ cm}^{-1} \text{ l. mol}^{-1}$]. Under the experimental conditions, the observed first-order rate constant for equilibrium attainment, k_{obsd} , is given by¹

$$k_{\text{obsd}} = k_1[\text{NaOCH}_3] + k_2 \quad (2)$$

where k_1 is the second-order rate constant for the formation of the complex and k_2 is the first-order rate constant for its decomposition. Table I contains the data for the attainment of equilibrium 1 for complex **3** at 13.45, 25.00, and 35.00° as a function of sodium methoxide concentration. From the slopes of plots of k_{obsd} vs. $[\text{NaOCH}_3]$, M , values for k_1 have been obtained and are given in Table I. The value for k_2 is very small and

(12) The analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(13) The carbon content of Meisenheimer complexes has been found to be low in several other cases.^{1,14} Since complex **3** is spectroscopically pure, the low carbon analyses may be due to the loss of methanol or the presence of carbonate in the ash.

(14) E. Bergman, N. R. McFarlane, and J. J. K. Boulton, *Chem. Commun.*, 511 (1970).

(15) J. F. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969).

(16) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). The program is available from Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

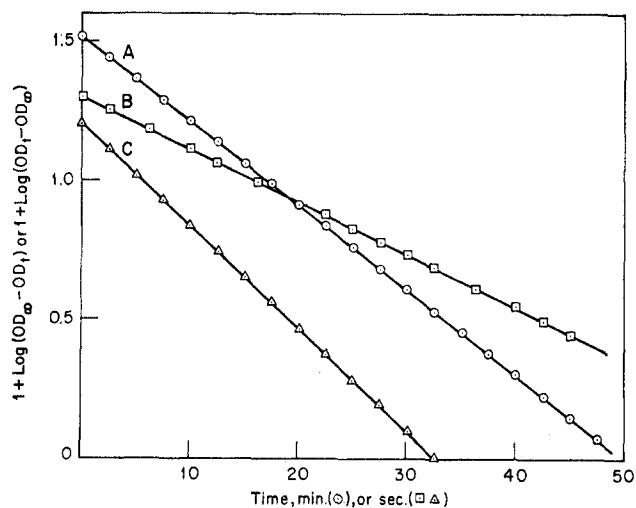


Figure 1.—(A) Plot of $\log (OD_t - OD_\infty)$ against time for the decomposition of **3** in methanol at 25.00°. (B and C) Plots of $\log (OD_\infty - OD_t)$ against time for the attainment of equilibrium for **3** in methanol at 25.00°, $[\mathbf{3}] = 3.34 \times 10^{-5} M$, for (B) $[\text{NaOCH}_3] = 1.32 \times 10^{-2} M$ and for (C) $[\text{NaOCH}_3] = 2.64 \times 10^{-2} M$.

interpolation from the intercepts of the plots is impossible. We have obtained k_2 values, however, directly from decomposition of solid **3** in methanol at the appropriate temperatures. The obtained k_2 , and hence K , values are also given in Table I.

TABLE I
INTERACTION OF 1-METHOXY-2,4,5-TRINITRONAPHTHALENE
($3.34 \times 10^{-5} M$) WITH METHANOLIC SODIUM METHOXIDE

Temp, °C	$10^4[\text{NaOCH}_3]$, M	$10^3 k_{\text{obsd}}$, sec ⁻¹	k_1 , M ⁻¹ sec ⁻¹ ^a	$10^4 k_2$, sec ⁻¹ ^b	$10^{-4} K$, l. mol ⁻¹ ^c	
13.45	0.00		13.75	2.88	4.77	
	16.5	2.24				
	33.0	5.11				
	41.3	5.19				
	57.9	7.59				
	66.0	8.74				
	74.4	10.1				
	82.7	11.1				
	25.00	0.00		32.8	11.2	2.93
		3.31	0.805			
4.13		1.27				
4.96		1.72				
6.62		2.02				
8.27		2.42				
9.91		2.87				
13.2		4.30				
16.5		5.52				
19.8		6.80				
35.00	0.00		59.7	27.2	2.19	
	3.31	1.40				
	4.14	2.44				
	6.61	3.90				
	8.27	4.37				
	9.93	5.89				
	13.2	7.80				
	19.8	11.5				
	26.4	15.9				

$$E_1 = 12.2 \pm 0.8 \text{ kcal mol}^{-1}, E_2 = 18.6 \pm 0.8 \text{ kcal mol}^{-1}, \Delta S_1^\ddagger = -12.5 \pm 2.0 \text{ eu}, \Delta S_2^\ddagger = -11.7 \pm 2.0 \text{ eu}^d$$

^a Obtained from the slope of k_{obsd} vs. $[\text{NaOCH}_3]$, M . ^b Mean of six runs (each within $\pm 3\%$) obtained by following the decomposition of the solid complex **3** in methanol. ^c $K = k_1/k_2$. ^d At 25.00°.

Data for the decomposition of **3** in aqueous solutions at different pH values are given in Table II.

TABLE II
DECOMPOSITION OF THE METHOXYL COMPLEX OF
1-METHOXY-2,4,5-TRINITRONAPHTHALENE (**3**)
IN WATER AT 25.00°

pH ^a	10 ³ k ₂ , sec ⁻¹	10 ⁻³ k ₂ H ⁺ , M ⁻¹ sec ⁻¹ ^b
5.38	5.63	1.32
5.44	5.06	1.35
5.46	4.68	1.32
5.49	4.54	1.36
5.58	4.21	1.54
5.64	3.28	1.36
5.75	2.49	1.31
6.07	1.32	1.37
6.30	0.90	1.48
8.07 ^c	0.22	
10.44 ^d	0.157	
10.55 ^d	0.163	
10.96 ^d	0.157	

^a 0.01 M KH₂PO₄ buffer, except where stated otherwise.
^b $k_2^{H^+} = k_2^{obsd} - k_2^0/[H^+]$, where $k_2^0 = 1.59 \times 10^{-4}$ sec⁻¹.
^c 0.01 M Na₂HPO₄ buffer. ^d 0.005 M Na₂HPO₄ buffer.

In methanol **5** undergoes solvolysis to give the corresponding naphthol; the half-life for this "solvolysis" is, however, several orders of magnitude less than the time scale used in the present work.⁸ The slow decomposition of **3** also produces naphthol, but its extinction coefficient at 500 nm is negligible compared to that of **3** and therefore does not interfere with the rate measurements.

The pmr parameters for 1-methoxy-2,4,5-trinitronaphthalene (**5**) and for the 1,1 complex of **3** in DMSO-*d*₆ and DMA solutions are given in Table III.

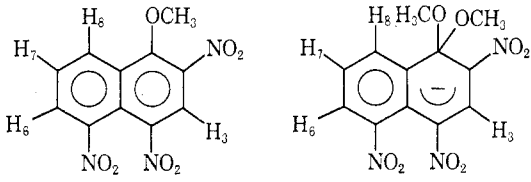
Discussion

The order of stability of Meisenheimer complexes parallels the extent of electron delocalization caused by substituents. It is instructive to compare the kinetic and thermodynamic parameters for the formation and decomposition of the 2,4-dinitro- (**2**)^{5,17} and 2,4,6-trinitro- (**7**)¹⁷ substituted 1,1-dimethoxycyclohexadienylidions with those of their 2,4-dinitronaphthalene (**1**) and 2,4,5-trinitronaphthalene (**3**) analogs. The equilibrium constants for the formation of the complexes increase in the order **3** > **7** >> **1** >> **2**¹⁸ (at 25.00°, $K_2 \approx 10^{-4}$; $K_1 = 230$; $K_7 = 17,000$; and $K_3 = 29,300$ l. mol⁻¹). More significantly, however, the introduction of a third nitro group in the 6 position of 2,4-dinitroanisole enhances the complex stability by a factor of 10⁸ (K_7/K_2) whereas the corresponding increase in the equilibrium constant resulting from an additional nitro group in the 5 position of 1-methoxy-2,4-dinitronaphthalene is only 127 (K_3/K_1). These results are not unexpected⁷ and can be rationalized in terms of the differences between the position of the nitro groups in the parent ethers of **3** and **1**. The 5-nitro group in 1-methoxy-2,4,5-trinitronaphthalene (**5**) is further removed from the seat of substitution than the 6-nitro group in 2,4,6-trinitroanisole and hence its

(17) J. H. Fendler, *J. Amer. Chem. Soc.*, **88**, 1237 (1966).

(18) The value reported by Katsanos for K_3 (1.76×10^3 l. mol⁻¹ at 34.9°) is clearly too low and probably in error due to the experimental uncertainties involved in its estimation.⁸

TABLE III
PMR PARAMETERS FOR
1-METHOXY-2,4,5-TRINITRONAPHTHALENE AND
ITS METHOXYL MEISENHEIMER COMPLEX^a



Solvent	5		3^b	
	DMSO- <i>d</i> ₆	DMA	DMSO- <i>d</i> ₆	DMA
τ_3	1.08 ^c	0.93 ^c	0.92 ^c (0.92) ^c	0.73 ^c (0.74) ^c
τ_6	1.18	1.02	2.07 (2.05)	1.96 (1.95)
τ_7	1.92	1.81	2.62 (2.63)	2.58 (2.57)
τ_8	1.36	1.24	2.14 (2.15)	2.09 (2.10)
τ_{1-OCH_3}	5.81 ^c	5.63 ^c	7.20 ^c (7.17) ^c	7.12 ^c (7.10) ^c
J_{67}	8.7	8.6	8.1 (8.1)	8.0 (8.0)
J_{68}	1.2	1.1	1.4 (1.4)	1.4 (1.5)
J_{78}	7.8	7.8	7.9 (7.7)	7.7 (7.7)

^a Calculated from the resonance frequencies observed at 50-Hz sweep widths using LAOCOON III (see Experimental Section) unless specified otherwise. ^b Values in parentheses have been obtained in the *in situ* formation of **3** by the dropwise addition of 5.05 M potassium methoxide in methanol to a solution of **5** in the indicated solvent. ^c Taken from spectra determined at 500-Hz sweep widths.

inductive effect results in a substantially smaller decrease in the electron density at C-1. Additionally, the proximity of the 4- and 5-nitro groups in **5** most probably decreases the extent of conjugation by steric hindrance,¹⁹ and thus the activating power of both groups, as well as resulting in lesser resonance stabilization of complex **3**.²⁰ In the case of 2,4,6-trinitroanisole and its complex **7**, on the other hand, the nitro group in the 6 position activates C-1 inductively, and all three nitro groups delocalize the negative charge of the cyclohexadienylidion by resonance effects. The significant electron delocalizing influence of the second aromatic ring in **3** results, however, in an overall increase in the equilibrium constant for the formation of **3** compared to that for **7**. The full extent of this effect can easily be appreciated by comparison of the stabilities of **1** and **2** ($K_1/K_2 \approx 2 \times 10^6$).

The higher equilibrium constant for **3** compared to that for **1** is a consequence of a significant increase in the rate constant for the formation of **3** (k_1 for **3**/ k_1 for **1** = 35.6) which is paralleled by a smaller decrease in the rate constant for its decomposition (k_2 for **1**/ k_2 for **3** = 3.5). Changes in the equilibrium constants for the complexes derived from the isomeric 2,4,6-cyanodinitro and dicyanonitroanisoles, on the other hand, are dependent to a greater extent on changes in k_2 than those in k_1 .¹ Although the available data are not

(19) V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966).

(20) We are currently studying the rates and equilibrium constants for the formation of tri- and tetranitro-substituted naphthalene Meisenheimer complexes to substantiate quantitatively this postulate.²¹

(21) E. J. Fendler and J. H. Fendler, unpublished work.

sufficiently extensive to justify generalizations, it appears that substituents with different electron-withdrawing ability exert a greater effect on k_2 than on k_1 , whereas the reverse is the case if the extent of electron-delocalization is altered by the introduction of the same functional group.

The greater stability of **3** compared to **1** is a consequence of a decrease in the energy and an increase in the entropy of activation for the formation of the complex. Similarly, decomposition of **3** requires somewhat more energy and has a higher entropy of activation than **1**.⁴ In many instances it has been found that the driving force for the formation and decomposition of complexes is both enthalpy and entropy dependent.¹

The greater stability of **3** relative to **1** is further demonstrated by the rate constant for its decomposition in water (k_2° in Table II) which is a factor of 11-fold smaller than that for **1** (k_2° for **1** at 25.0° = $1.76 \times 10^{-3} \text{ sec}^{-1}$).⁴ This reaction like the analogous decomposition of **1**⁴ and **7**²² is catalyzed by hydronium ions, although this catalysis is smaller ($k_2^{\text{H}^+}$ = $1.38 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ for **3**) than that observed for **1**⁴ ($k_2^{\text{H}^+}$ = $1.73 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$) or for **7**²¹ ($k_2^{\text{H}^+}$ = $4.0 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$).

We continue to use proton magnetic resonance spectroscopic techniques to confirm the postulated structure of the intermediate **3** and to observe its formation *in situ* by the addition of methoxide ions to solutions of **5** in DMSO- d_6 and in DMA. The only previous reports of pmr data for naphthalene Meisenheimer complexes are those on **1**^{4,23} and other 1-alkoxy-2,4-dinitronaphthalenes.^{4,24} No pmr data has previously been reported, however, for Meisenheimer complexes of trinitronaphthalenes.

The pmr parameters for the complex **3** and its parent ether **5** as well as those observed previously⁸ for complex **1** and the parent are given in Table III. The spectra of **3** are completely consistent with the postulated structure (*i.e.*, the 1,1 complex) and eliminate the possibility of alternative complexes such as those resulting from attack of methoxide ion at C-3, C-6, or C-8. Pmr criteria for the structure of Meisenheimer complexes have been discussed previously^{1,2,4,10,15,24} and therefore are not reiterated here in detail. Rehybridization of C-1 from sp^2 in the parent ethers to sp^3 in the 1,1 complexes has been found to result in an upfield shift of the methoxy proton resonances in dinitro-, trinitro-, and cyanonitroanisoles ($\Delta\delta$ 1.00–1.50 ppm)^{1,2,10,15} and in 1-methoxy-2,4-dinitronaphthalene ($\Delta\delta$ 1.33–1.35 ppm).⁴ A comparable upfield shift of the methoxyl resonance ($\Delta\delta$ 1.39 ppm in DMSO- d_6 and 1.49 ppm in DMA) is observed for **5**. It has also been observed previously that the aromatic proton resonances of Meisenheimer complexes are relatively strongly shielded as compared to the parent ethers^{1,2,4,10,15,24} and that the magnitude of the upfield shift ($\Delta\delta$) for 1,1-dialkoxy-2,4-dinitrocyclohexadienylides¹⁰ reflects the relative charge densities at the various positions, *i.e.*, H-3, 0.04–0.07; H-5, 1.26–1.40; H-6, 2.50–2.57 ppm. The aromatic proton resonances of the second ring of **3** and **5** comprise an ABX system whereas those of the dinitronaphthalenes **1** and **6** compose a less readily interpretable ABCD

system.⁴ The aromatic proton resonances of the ether **5** consist of a one-proton singlet (H-3) at τ 1.08 and three one-proton doublets of doublets centered at τ 1.16 (H-6), 1.36 (H-8), and 1.95 (H-7) in DMSO- d_6 solution (see Table III for the calculated chemical shifts of H-6, H-7, and H-8). The aromatic resonances of complex **3** resemble those of **5** in terms of multiplicity but the chemical shifts are altered markedly. The H-6, H-7, and H-8 resonances show the expected upfield shifts: H-6, τ 2.07 ($\Delta\delta$ 0.89); H-7, 2.62 ($\Delta\delta$ 0.70); and H-8, 2.14 ppm ($\Delta\delta$ 0.78); but the magnitude of the upfield shifts are considerably smaller than those cited previously for the three ring protons of benzene complexes. These smaller shifts are explicable in terms of delocalization of the negative charge over more atoms in **3** than in the benzene complexes. The H-3 resonance, however, is shifted downfield to τ 0.92 ppm ($\Delta\delta$ -0.16 ppm). The shifts of the aromatic protons of **3** indicate a significant increase in electron density at the 6, 7, and 8 positions of the complex relative to the parent ether **5** but a decrease in electron density at the 3 position. The increase in electron density is expected but the similarity in the increase at H-6, H-7, and H-8 is not readily explicable in terms of canonical contributions and anisotropic deshielding of H-8 by the methoxyl groups of the complex. HMO calculations of π -electron densities of **6** and its methoxyl complex **1** indicate that there is a slight increase in electron density in the second ring, and that the negative charge is primarily localized in the nitro groups.²⁵ The electron density in the first ring, therefore, should be markedly decreased, *i.e.*, at H-3, in the complex relative to the parent ether. Our observed $\Delta\delta$ values are in qualitative agreement with the results of these HMO calculations.

The proton chemical shifts of **3** and **5** show only a slight dependence on the dipolar aprotic solvent used, *i.e.*, DMSO- d_6 and DMA (Table III). In general, the proton resonances are observed at lower fields in DMA than in DMSO- d_6 for both the parent ether **5** and its complex **3**; consequently the magnitude of the chemical shift differences ($\Delta\delta$) between **5** and **3** are quite similar in these two solvents.

In several activated aromatic systems, *i.e.*, 2,4,6-trinitroanisole,^{15,26,27} isomeric cyanodinitroanisoles,¹⁵ 2,4-dicyano-6-nitroanisole,¹ and 3,5-dinitro-2-methoxy-pyridine,²⁸ initial attack of the nucleophile has been observed by pmr^{1,15,26–28} and calorimetric²⁹ techniques to occur at C-3 resulting in the formation of a transient 1,3 complex. However, on a considerably shorter time scale, the presence of other transient species and the formation of the 1,3-methoxyl complex of 1-methoxy-2,4-dinitronaphthalene (**6**) has been inferred from kinetic data obtained by the use of stopped-flow techniques.³⁰ In order to observe any fairly stable transient species in the interaction of methoxide ions with **5**, we examined the generation of **3** *in situ* in

(25) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).

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DMSO- d_6 and in DMA.³¹ In these experiments, no additional resonances could be observed and, hence, on the time scale necessitated by pmr techniques at 25° (~2.5 min),^{1,15} the 1,3 complex of **5** is either not formed or is not detectable.

(31) DMA has been found to considerably enhance the stability of the 1,3-dimethoxy-2,4,6-trinitrocyclohexadienylidene ion as compared to that in DMSO.³² However, no 1,3-complex formation could be detected in the *in situ* formation of complex **1** from **6** either in DMSO- d_6 or in DMA.

Registry No.—**3**, 25734-07-0; **5**, 25599-63-7.

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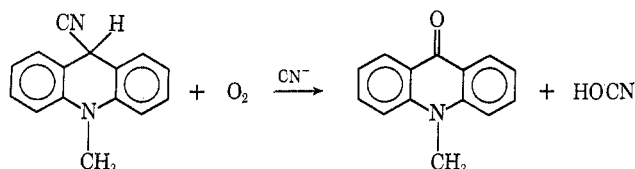
Electron Spin Resonance Studies of Radical Formation in Nucleophilic Addition Reactions. III. On the Mechanism of Radical Formation and Chemiluminescence in the Cyanide Addition and Oxygenation of *N*-Methylacridinium Chloride¹

JOHN W. HAPP, EDWARD G. JANZEN,* AND BRUCE C. RUDY

Department of Chemistry, The University of Georgia, Athens, Georgia 30601

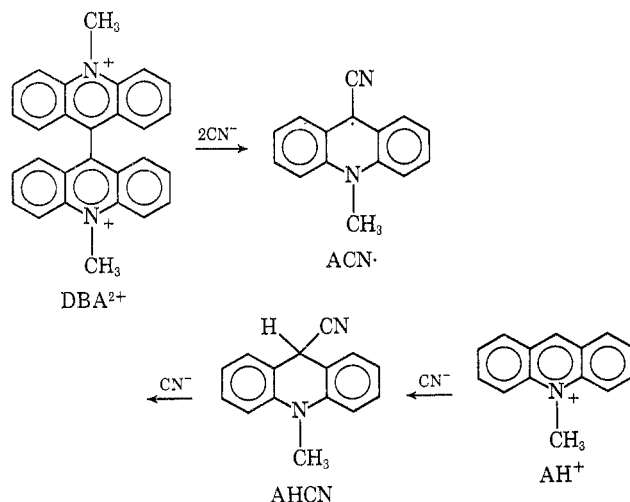
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The reaction of KCN with *N*-methylacridinium chloride in 90% dimethyl sulfoxide–10% water produces *N*-methyl-9-cyanoacridan. With excess cyanide the red *N*-methyl-9-cyanoacridanide anion is produced. In the presence of oxygen *N*-methylacridone and potassium cyanate are produced with light emission. The reaction stoichiometry is shown to be



The initial rate of oxygen uptake shows the same dependence on the potassium cyanide concentration as the maximum light emission intensity on this variable and the time required to reach the light emission maximum is about the same as the time required for the major portion of the oxygen to be absorbed in the same experiment. The significance of these observations is discussed. In these experiments *N*-methyl-9-cyanoacridanyl is detected. A carbanion electron transfer oxidation mechanism involving this radical as an intermediate is suggested.

In a previous report² we described the detection of *N*-methyl-9-cyanoacridanyl radical in the cyanide ion addition to oxygen free solutions of lucigenin (*N,N'*-dimethyl-9,9'-biacridinium dinitrate) or to air-saturated solutions of *N*-methylacridinium chloride. The structure of the radical was verified by electrolytic reduction of *N*-methyl-9-cyanoacridinium chloride. The esr



spectrum was analyzed and coupling constants assigned on the basis of molecular orbital calculations and by analogy to radicals of similar structure.

The unusual reaction between cyanide ion and *N*-methylacridinium chloride to produce *N*-methyl-9-cyanoacridanyl radicals (ACN·)³ in air-saturated solutions has been investigated in more detail. Reactions of *N*-methyl-9-cyanoacridan (AHCN) and the chemiluminescent production of *N*-methylacridone have also been studied.

Experimental Section

Equipment.—The esr and light detection equipment was the same as used for a previous study.⁴ Relative chemiluminescence light emission was monitored using a Firefly photometer with a IP21 photomultiplier tube. Solutions of *N*-methylacridinium chloride were placed in the sample compartment of the photometer and an appropriate amount of potassium cyanide in the same solvent was injected by syringe into the solution so that the final volume of the reaction mixture was 5 ml. Oxygen was continuously bubbled through the reaction mixture and the intensity of chemiluminescence was recorded. Chemiluminescence spectra were obtained with an Aminco spectrofluorometer equipped with a xenon arc light and a IP28 photomultiplier tube. A typical solution contained 0.04 *M* *N*-methylacridinium chloride and 0.06 *M* potassium cyanide in 90% dimethyl sulfoxide–10% water (by volume) saturated with oxygen.

(3) For abbreviation, "A" is used as the symbol for the *N*-methylacridanyl moiety. "A" is followed by symbols representing the substituent(s) in the 9 position of the acridine ring.

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* Author to whom correspondence should be addressed.

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