

The Elusive 1,1-Meisenheimer Complex from 2,4,6-Trinitroanisole and Aryloxide Ions. A Stopped-Flow Temperature-Jump Study¹

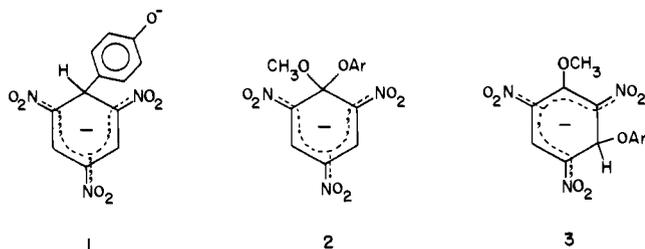
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Abstract: 2,4,6-Trinitroanisole (TNA) and phenoxide ion form a transient complex with a lifetime of a few seconds in Me₂SO-water solutions. Evidence is presented to show that this transient species is the Meisenheimer complex 1-methoxy-1-phenoxy-2,4,6-trinitrocyclohexadienate, formed by the attack of phenoxide ion through oxygen on the 1 position of TNA. It is rapidly converted into another Meisenheimer complex formed by hydroxide ion attack on the 3 position of TNA. The kinetics of the phenoxide ion complex formation was investigated by the stopped-flow temperature-jump relaxation technique in 50, 60, 70, 80, and 90% aqueous Me₂SO. Plots of the logarithm of the rate constant for complex formation and for complex dissociation vs. the mole fraction of Me₂SO are linear; this permits extrapolation of the rate constants to water solution. Phenoxide ion departure is found to be more than 10⁶ times faster than methoxide ion departure from the corresponding 1,1-dimethoxy Meisenheimer complex in aqueous solution, whereas the rates of phenoxide and methoxide ion attack on TNA are very similar. The kinetics of complex formation between TNA and various substituted phenoxide ions was also measured in 90% Me₂SO-10% water. Aryloxide ion departure was found to depend fairly strongly on the pK_a of the respective phenol, with an approximate β_{1g} ≈ -0.7.

A large fraction of recent and current research efforts in the field of S_NAr reactions has been directed toward the structural, thermodynamic, and kinetic characterization of Meisenheimer complexes.² Some of the most thoroughly characterized complexes include those formed by the attack of an alkoxide ion on activated aromatics.

In contrast to alkoxide ion complexes, it has been much more difficult to generate and prove the structure of the corresponding aryloxide complexes. Shein et al.³ reported phenoxide ion attack on 1,3,5-trinitrobenzene, at the 1 position of 2,4,6-trinitroanisole, and at the 1 and 3 positions of 2,4,6-trinitrophenylphenyl ether in Me₂SO. Buncl et al.,⁴ however, could not reproduce Shein's results with 1,3,5-trinitrobenzene; they reported the formation of **1** instead where phenoxide ion



attack occurs through its para carbon. In a more recent paper Shein⁵ reports the observation, again in Me₂SO, of **1** as a thermodynamic product which is preceded by the formation of the kinetically controlled complex in which phenoxide ion attacks via its oxygen atom.

In protic or partially protic solvents no evidence for phenoxide ion attack via oxygen has been reported to date. We now describe a kinetic study of the interaction between 2,4,6-trinitroanisole (TNA) and phenoxide ion in 50, 60, 70, 80, and 90% aqueous Me₂SO and also between TNA and substituted phenoxide ions in 90% aqueous Me₂SO, and present evidence for the formation of **2** as a transient species.

Results and Discussion

When TNA is mixed with a phenol-phenoxide ion buffer in a solvent containing at least 50% Me₂SO one observes the immediate formation of a transient complex whose spectrum is typical of a Meisenheimer complex (Figure 1). Under most conditions the formation of the complex is faster than the

mixing time of our stopped-flow apparatus. The spectrum in Figure 1 had to be determined in the stopped-flow apparatus because the complex is converted into what appears to be a second Meisenheimer complex (with a very similar but not identical spectrum) within a few seconds, which in turn slowly decomposes to picrate ion.

If the reaction solution is subjected to a temperature jump a few hundred milliseconds after mixing, a relaxation effect is observed with a relaxation time in the millisecond range. The amplitude of this relaxation effect decreases as the application of the temperature jump is further delayed; for example, in 80% Me₂SO, the effect becomes undetectable after 5-10 s, indicating complete disappearance of the transient complex.

Temperature-jump relaxation times were determined under pseudo-first-order conditions with TNA as the minor component. In order to suppress OH⁻ formation as much as possible, phenol was added to the reaction solution. The ionic strength was kept constant at 0.25 M with tetramethylammonium chloride.

The results are summarized in Table I; they indicate a concentration dependence like

$$1/\tau_1 = k_1[\text{ArO}^-] + k_{-1} \quad (1)$$

which is consistent with the formation of either **2** or **3**. Since the experiments were carried out at a constant [PhO⁻]:[PhOH] ratio, the phenoxide ion dependence is authentic and does not represent a disguised hydroxide ion dependence (PhO⁻ + H₂O ⇌ PhOH + OH⁻); this is further confirmed by the fact that a change in the [PhO⁻]:[PhOH] ratio from 4:1 to 1:1 (experiments in 80% Me₂SO) has no effect on 1/τ₁. Note that in Me₂SO-poor solvent mixtures (50 and 60%) 1/τ₁ is concentration independent, indicating k₋₁ ≫ k₁[ArO⁻].

The rate constants are summarized in Table II. In 70, 80, and 90% Me₂SO they were obtained from the slope (k₁) and intercept (k₋₁) of plots according to eq 1; in 50 and 60% Me₂SO, k₁ was calculated indirectly from k₋₁ and K₁, the latter being estimated spectrophotometrically (see Experimental Section).

In view of the known tendency of phenol and phenoxide ion to associate⁶ according to



the question arises whether such association could significantly

Table I. Reciprocal Relaxation Time ($1/\tau_1$)^a for the Reaction of TNA with Tetramethylammonium Phenoxide in Aqueous Me₂SO at 25 °C.^b

[PhO ⁻], M	[PhOH], M	50% Me ₂ SO ^c	60% Me ₂ SO ^c	70% Me ₂ SO ^c	80% Me ₂ SO ^c	90% Me ₂ SO ^{c,d}
0.001	0.00025					180 ± 25
0.002	0.0005					275 ± 30
0.005	0.00125					485 ± 40
0.01	0.0025			380 ± 30	365 ± 25	675 ± 75
0.02	0.005			400 ± 35	410 ± 30	
0.05	0.0125		630 ± 70	440 ± 45	500 ± 30	
0.05	0.05 ^e				510 ± 30	
0.10	0.025	850 ± 100	660 ± 70	500 ± 50	700 ± 40	
0.10	0.10 ^e				650 ± 40	

^a In s⁻¹. ^b Ionic strength 0.25 M (Me₄NCl). ^c Volume percent. ^d 30 °C. ^e [PhO⁻]:[PhOH] = 1:1, all others 4:1.

Table II. Rate and Equilibrium Constants for the Reaction of TNA with Tetramethylammonium Phenoxide in Aqueous Me₂SO at 25 °C^a

% Me ₂ SO	N _{Me₂SO} ^b	k ₁ , M ⁻¹ s ⁻¹	k ₋₁ , s ⁻¹	K ₁ , M ⁻¹
0	0	80 ^c	1900 ^c	0.042 ^{c,f}
50	0.205	425 ^e	850	0.5 ^d
60	0.275	645 ^e	645	1.0 ^d
70	0.370	1200	380	3.2 ^f
80	0.500	3600	320	10.9 ^f
90	0.725	50 000 ^g	175 ^g	285 ^{f,g}

^a Estimated error limits 10–20%. ^b Mole fraction. ^c Extrapolated; see text and Figure 2. ^d Determined spectrophotometrically. ^e Calculated as $k_1 = K_1 k_{-1}$. ^f Calculated as $K_1 = k_1/k_{-1}$. ^g At 30 °C.

affect our results. The linearity of the plots of $1/\tau_1$ vs. phenoxide ion concentration and the absence of a significant effect on $1/\tau_1$ when the [PhO⁻]:[PhOH] ratio is changed from 4:1 to 1:1 shows that the association is minor or that the nucleophilic reactivity of PhO–H...O⁻Ph is not much different from that of free phenoxide ion. It should also be noted that since the [PhO⁻]:[PhOH] ratio was 4:1 in most experiments, not more than 25% of the phenoxide ion could possibly be tied up; this could lead to no more than a 25% reduction in the k_1 step (assuming zero reactivity of PhOH...O⁻Ph) in any event.

1,1 or 1,3 Complex? There are several pieces of evidence which indicate that our transient complex must be the 1,1 complex **2** rather than the 1,3 complex **3**. (1) In pure Me₂SO there is NMR evidence that the initial complex formed is **2**.⁷

(2) The ratio of the extinction coefficients of the two maxima in the absorption spectrum, $\epsilon_1/\epsilon_2 = 1.46$, is close to that of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate ion (1.48, Figure 1) and other typical 1,1-dialkoxy-2,4,6-trinitrocyclohexadienate ions (1.48–1.52),^{2a} but quite different from that of 1,3-dimethoxy-2,4,6-trinitrocyclohexadienate ion (1.30, Figure 1) or that of 1,3-diethoxy-2,4,6-trinitrocyclohexadienate ion (1.26).⁸

(3) If the transient complex were **3** instead of **2**, one would expect to see the formation of the more stable **2** in a slower subsequent reaction, in analogy to the reaction of TNA with methoxide ion,⁹ and many similar examples.^{2a–d} The concentration dependence of the second relaxation time would be given by

$$1/\tau_2 = \frac{k_2[\text{ArO}^-]}{1 + K_1[\text{ArO}^-]} + k_{-2} \quad (3)$$

where K_1 is the equilibrium constant for the formation of **3**, and k_2 and k_{-2} refer to **2**.

We have in fact observed a second relaxation process, but it has the “wrong” concentration dependence. The data are summarized in Table III; despite a large experimental error, due to very small OD changes, we can detect a clear decreasing

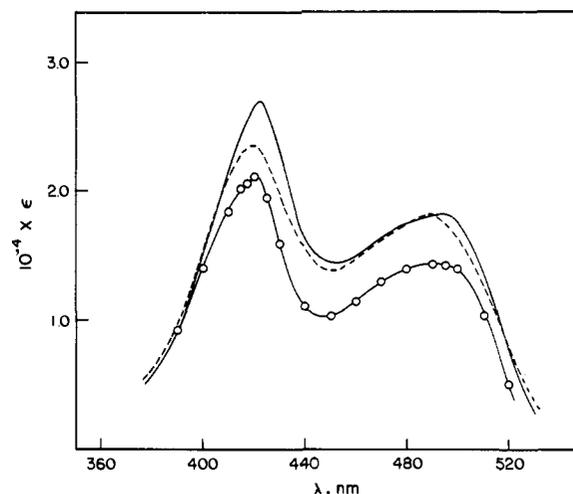


Figure 1. Absorption spectra of Meisenheimer complexes. –O–O–, **2** in 99% Me₂SO–1% water; —, TNA–MeO⁻ 1,1 complex in 96% Me₂SO–4% methanol; - - -, TNA–MeO⁻ 1,3 complex in 96% Me₂SO–4% methanol.

trend in $1/\tau_2$ with increasing [ArO⁻] (runs 1–3, 4–6) and an increasing trend with increasing [OH⁻] (runs 1 and 4, 2 and 5, 3 and 6). These results are inconsistent with eq 3; they are most easily explained by a scheme in which the rapid formation of **2** is followed by a slower attack of hydroxide ion at the 3 position (or perhaps the 1 position) of TNA to form the corresponding hydroxide complex.

(4) The fourth piece of evidence is based on a comparison of the rate constants for various phenoxide and methoxide Meisenheimer complexes, as discussed in the following section.

Solvent Dependence of Kinetic Parameters. Figure 2 shows the dependence of $\log k_1$ and $\log k_{-1}$ on the mole fraction of

Table III. Reciprocal Relaxation Time ($1/\tau_2$) for the Slow Process in 80% Me₂SO at 25 °C^a

run	[PhO ⁻], M	[PhOH], M	[PhO ⁻]/ [PhOH]	[OH ⁻], ^b M	$1/\tau_2$, s ⁻¹
1	0.01	0.01	1	$\sim 4.2 \times 10^{-6}$	0.35 ± 0.05
2	0.02	0.02	1	$\sim 4.2 \times 10^{-6}$	0.21 ± 0.05
3	0.05	0.05	1	$\sim 4.2 \times 10^{-6}$	0.23 ± 0.05
4	0.01	0.0025	4	$\sim 1.8 \times 10^{-5}$	0.49 ± 0.05
5	0.02	0.005	4	$\sim 1.8 \times 10^{-5}$	0.47 ± 0.05
6	0.05	0.0125	4	$\sim 1.8 \times 10^{-5}$	0.34 ± 0.05

^a Ionic strength 0.25 M (Me₄NCl). ^b From pH measurements and calculated as $\log [\text{OH}^-] = \text{pH} - \text{p}K_s$ with $\text{p}K_s$ from J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 1851 (1969); the absolute [OH⁻] values are only approximate since pH and $\text{p}K_s$ refer to different ionic strengths and temperatures.

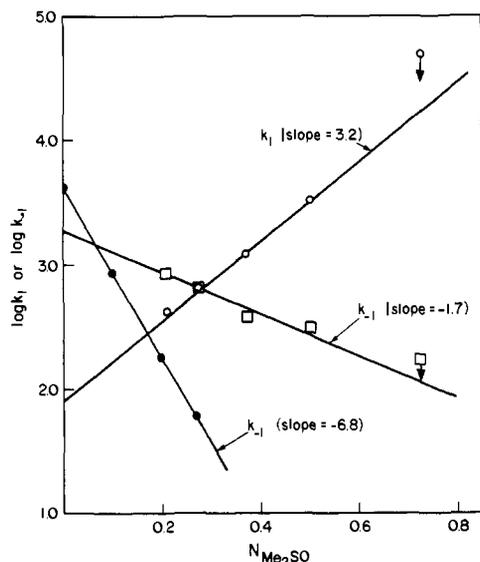


Figure 2. Dependence of k_1 and k_{-1} on the mole fraction of Me_2SO . \circ , k_1 for **2**; \square , k_{-1} for **2**; \bullet , k_{-1} for TNA- MeO^- 1,1 complex. Points with arrows deviate because of higher temperature.

Table IV. Kinetic Parameters for Phenoxide and Methoxide Complexes with TNA at 25 °C

	TNA- PhO^- 1,1 complex	TNA- MeO^- 1,1 complex	TNA- MeO^- 1,3 complex
$k_1, \text{M}^{-1} \text{s}^{-1}$	50 (H_2O) ^a	17 (MeOH) ^b	950 (MeOH) ^c
k_{-1}, s^{-1}	1900 (H_2O) ^a	10^{-3} (MeOH) ^b 4.2×10^{-4} (H_2O) ^a	350 (MeOH) ^c
K_1, M^{-1}	0.026 (H_2O) ^a	17 000 (MeOH) ^b	2.71 (MeOH) ^c
$k_1^{\text{PhO}^-}/k_1^{\text{MeO}^-}$		2.94 ^d	5.26×10^{-2} ^e
$k_{-1}^{\text{PhO}^-}/k_{-1}^{\text{MeO}^-}$		4.52×10^6 ^d	5.42 ^e
$K_1^{\text{PhO}^-}/K_1^{\text{MeO}^-}$		1.53×10^{-6} ^d	0.96×10^{-2} ^e

^a This work. ^b E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969). ^c Reference 9b. ^d Assuming the TNA- PhO^- complex is a 1,1 complex. ^e Assuming the TNA- PhO^- complex is a 1,3 complex.

Me_2SO . The plots are linear as previously observed for ethoxide ion departure from 1,1-diethoxy-2,4,6-trinitrocyclohexadienyl ion¹⁰ and for the reactions of certain spiro Meisenheimer complexes.¹¹ In order to further demonstrate the generality of these linear plots we have also determined the solvent dependence of the rate of methoxide ion departure from the 1,1-dimethoxy-2,4,6-trinitrocyclohexadienyl ion (Figure 2). Similar plots in Me_2SO -methanol mixtures for a variety of methoxide Meisenheimer complexes are equally linear,¹² which shows this to be a general phenomenon.

Based on the above it appears that extrapolation of our kinetic data to $N_{\text{Me}_2\text{SO}} = 0$ should yield fairly reliable rate constants in aqueous solution. These extrapolated values are summarized in Table IV along with similar data for the 1,1 and 1,3 complex between TNA and methoxide ion.

If one assumes that our TNA- PhO^- complex is the 1,1 complex, **2**, a comparison with the TNA- MeO^- 1,1 complex implies that phenoxide ion attack (k_1) is about three times faster than methoxide ion attack, that the phenoxide complex is about 6.5×10^5 less stable (K_1) than the methoxide complex, and that phenoxide ion departure (k_{-1}) is 4.5×10^6 times faster than methoxide ion departure. This is entirely consistent with known relative nucleophilicities of methoxide and phenoxide ion toward 1-substituted 2,4,6-trinitrobenzenes,¹³ and

Table V. Slopes for the Solvent Dependence for Various Meisenheimer Complexes.

complex	solvent	slope		
		k_1	k_{-1}	K_1^e
2,4,6-(NO_2) ₃ C_6H_2 - OPh^a	Me_2SO - H_2O	3.2	-1.7	4.9
2,4-(NO_2) ₂ C_6H_3 - O^-^b	Me_2SO - H_2O	8.8	-4.7	13.5
2,4,6-(NO_2) ₃ C_6H_2 - OMe^a	Me_2SO - H_2O		-6.8	
2,4,6-(NO_2) ₃ C_6H_2 - OEt^c	Me_2SO - H_2O		-6.7	
Various MeO^- -complexes ^d	Me_2SO - MeOH	3.5-5.0	-4.5 to -6.0	

^a This work. ^b Reference 11a. ^c Reference 10. ^d Reference 12. ^e Slope (K_1) = slope (k_1) - slope (k_{-1}).

with the frequently observed strong dependence of leaving group departure rates of alkoxide and aryloxy ions on the $\text{p}K_a$ of the corresponding alcohol.¹⁴

The alternative assumption that the TNA- PhO^- complex is the 1,3 complex, **3**, would imply that phenoxide ion departure from the 3 position is only about 5.4 times faster than methoxide ion departure from the same position and that the phenoxide complex is only about 104 times less stable than the corresponding methoxide complex (Table IV). This is completely unreasonable and without precedent.¹⁵

A further comment on the solvent dependence is in order. Even though the plots of $\log k$ vs. $N_{\text{Me}_2\text{SO}}$ are all linear for a variety of reactions, the slopes differ widely (Table V); these slopes are a measure of how much a rate (or equilibrium) constant would change in going from 0 to 100% Me_2SO , assuming that the linearity holds even at very high (>90%) Me_2SO concentrations. In aqueous Me_2SO the slope for k_{-1} becomes progressively more negative as the basicity of the leaving group increases and there seems to be an opposite trend for the slopes of k_1 and K_1 . It is generally recognized that a decrease in the solvation of the alkoxide ion by the protic solvent component is the main factor responsible for the effect of adding Me_2SO ,^{2a,2b,16} although stabilization of the complex and of the transition state by Me_2SO also plays an important role.^{16c,17} The trends in our slopes are consistent with the notion that solvation by the protic solvent is strongest for the most basic alkoxide ions (CH_3O^- , $\text{C}_2\text{H}_5\text{O}^-$) and weakest for the weakly basic phenoxide ion whose negative charge is more dispersed; these findings agree with data on solvent activity coefficients.^{16a,18} Comparison of the data in Me_2SO -water with those in Me_2SO -methanol further suggests that water is more effective in solvating alkoxide ions than methanol; this is again consistent with data on solvent activity coefficients^{16a,18} as well as with chemical intuition.

Reactions of Substituted Phenoxide Ions with TNA. We have also studied the kinetics of complex formation between TNA and a series of substituted phenoxide ions in 90% Me_2SO . The reaction is slow enough with *p*-methoxyphenoxide ion to be monitored by the stopped-flow technique; in all other cases the measurements had to be made by the stopped-flow temperature-jump method.

The data obey eq 1; the $k_1[\text{ArO}^-]$ term was significant only with *p*-methoxyphenoxide whereas with the other substituted phenoxides we found that $k_{-1} \gg k_1[\text{ArO}^-]$ under the conditions employed. In these latter cases k_1 was obtained from K_1 , determined spectrophotometrically, and k_{-1} . The results are summarized in Table VI.

Table VI. Rate and Equilibrium Constants for the Reaction of TNA with Tetramethylammonium Aryloxides in 90% Me₂SO at 30 °C.^a

substituent ^b	pK _a ^c	k ₁ , M ⁻¹ s ⁻¹	k ₋₁ , s ⁻¹	K ₁ , M ⁻¹
<i>p</i> -MeO ^d	16.14 ^j	6.0 ± 0.5 × 10 ⁴ ^{d,e}	50 ± 5 ^d	1200 ^f
H	15.42 ^j	5.0 ± 0.5 × 10 ⁴ ^g	175 ± 25	285 ^f
<i>p</i> -Cl	14.15 ^j	9.7 ± 1.0 × 10 ³ ^h	2.1 ± 0.1 × 10 ³	4.68 ^f
<i>p</i> -Br	14.10	8.7 ± 0.8 × 10 ³ ^h	2.5 ± 0.1 × 10 ³	3.47 ^f
<i>m</i> -Cl	13.58	3.1 ± 0.5 × 10 ³ ^h	4.0 ± 0.5 × 10 ³	0.77 ⁱ
<i>m</i> -Br	13.45	4.0 ± 0.5 × 10 ³ ^h	5.0 ± 0.7 × 10 ³	0.80 ⁱ

^a μ = 0.25 M ((CH₃)₄NCl), stopped-flow temperature-jump experiments. ^b Substituent of aryloxide ion. ^c pK_a of respective phenol extrapolated to zero concentration; see ref 19. ^d Stopped-flow experiments at 25 °C. ^e From slope according to eq 1, [ArO⁻] range 0.0005–0.002 M, [ArO⁻]:[ArOH] = 1:1. ^f Calculated as k₁/k₋₁. ^g From slope according to eq 1, [PhO⁻] range 0.001–0.01 M, [PhO⁻]:[PhOH] = 4:1. ^h Calculated as K₁k₋₁. ⁱ Determined spectrophotometrically. ^j At μ = 0 and zero concentration the pK_a values are 15.69, 15.05, and 13.82 for *p*-MeO, H, and *p*-Cl, respectively; J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 2047 (1970).

Brønsted-type plots of log k₁ and log k₋₁ vs. the pK_a of the respective phenols (not shown) are satisfactorily linear. The slopes of these plots are β_{nuc}(k₁) ≈ 0.60 and β_{lg}(k₋₁) ≈ -0.70. These slopes should be regarded as indicating orders of magnitude rather than precise values for the following reasons. Association of the type shown in eq 2 is probably fairly significant in 90% Me₂SO and under the conditions used with the bromo- and chlorophenoxides. This association is expected to reduce the nucleophilicity of the aryloxide ion and thus our k₁ values may be too low. It will also affect the pK_a values of the phenols; this is borne out by our findings that the pH of 1:1 phenol buffers depends significantly on buffer concentration.¹⁹

Even taking the above reservations and uncertainties into consideration it is clear that k₋₁ depends rather strongly on the pK_a of aryloxide. This is again consistent with the many data on leaving group departure rates discussed earlier.

Experimental Section

Materials. 2,4,6-Trinitroanisole was recrystallized thrice from methanol, mp 68–69 °C. Reagent grade phenol, *p*-chloro-, *m*-chloro-, *p*-bromo-, and *m*-bromophenol, and Me₂SO (stored over molecular sieves) were used without further purification; *p*-methoxyphenol was recrystallized from benzene. Potassium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienolate was prepared by standard procedures. Tetramethylammonium hydroxide solutions were titrated by standard procedures.

In establishing the percent content of Me₂SO of the reaction solutions, the ingredients were mixed with the required quantity of Me₂SO, and water was then added up to the mark of the volumetric flask at 20 °C. The pH measurements were carried out with a Corning Model 110 pH meter as described previously.²⁰

Spectra. The spectrum of **2** was taken in the stopped-flow spectrophotometer, a few hundred milliseconds after mixing TNA with a phenol-phenolate buffer in 99% Me₂SO–1% water. The spectra of the 1,1- and 1,3-TNA–MeO⁻ complexes were obtained on a Cary 14 spectrophotometer. The spectrum of the latter was taken about 2 min after mixing a solution of 2.6 × 10⁻⁵ M TNA with 8.0 × 10⁻⁴ M sodium methoxide in 96% Me₂SO–4% methanol. Under these conditions its conversion into the thermodynamically favored 1,1 complex⁹ has made little progress; we determined the pseudo-first-order rate coefficient for this conversion to be 2.42 × 10⁻⁴ s⁻¹, which means that at the time the spectrum was taken there was ≥95% of the 1,3 complex and ≤5% of the 1,1 complex in the reaction mixture. The spectrum of the 1,1 complex shown in Figure 1 is that of the above solution several hours after mixing; it is virtually identical with the spectrum of an authentic sample of potassium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienolate in the same solvent.

Determination of K₁. The equilibrium constant K₁ is given by

$$K_1 = \frac{\text{OD}}{[\text{ArO}^-]l\epsilon} \left([\text{TNA}]_0 - \frac{\text{OD}}{l\epsilon} \right)^{-1} \quad (4)$$

where OD is the optical density measured in the stopped-flow apparatus a few hundred milliseconds after mixing, *l* is the path length, and ε is the extinction coefficient of the complex at 490 nm, assumed to be 16 000²¹ in all cases.

Temperature-Jump Experiments. The kinetic experiments were done

in a Durrum D-115 stopped-flow temperature-jump apparatus. In a typical experiment a 2.5–3.0-kV pulse was applied to the reaction solution 100–200 ms after mixing. Depending on the solvent this produced a temperature jump of 8–11 °C. The relaxation was monitored at 490 nm; relaxation times were determined from the averaging of six oscilloscope traces.

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