trogen in an aromatic ring are, as expected, greatly influenced by the polar nature of any substituents, but the K_f value for pyridine (1.88) places them, as a group, among the most capable H acceptors.

It is quite obvious that, in collecting data from hundreds of different laboratories where a variety of techniques were used over a span of 90 years, a sizable number of erroneous values are to be expected in Tables III–XXIII.[15b] However, these "random errors" are certainly as likely in the butanol–water system as in any other, and yet the correlation between it and octanol–water is remarkably good ($r = 0.993$). We must conclude, therefore, that the majority of the deviations noted, for example in the $CHCl_3$–water system, are real and are subject to interpretation on the basis of how the solvent–solute forces differ from the reference system.

Accumulation of partition coefficient data is continuing, and future compilations of more accurate values should place the structural interpretations on an even firmer basis.

Registry No.—Cyclohexane, 110-82-7; heptane, 142-82-5; CCl_4, 56-23-5; xylene, 1330-20-7; toluene, 108-88-3; benzene, 71-43-2; $CHCl_3$, 67-66-3; nitrobenzene, 98-95-3; isopentyl acetate, 123-92-2; oleyl alcohol, 143-28-2; methyl isobutyl ketone, 108-10-1; ethyl acetate, 141-78-6; octanol, 111-87-5; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; cyclohexanol, 108-93-0.

Intermediates in Nucleophilic Aromatic Substitution. IX.[1,2] Kinetic and Proton Magnetic Resonance Investigations of the Interaction of Lyate Ions with *N-tert*-Butyl-2,4,6-trinitrobenzamide

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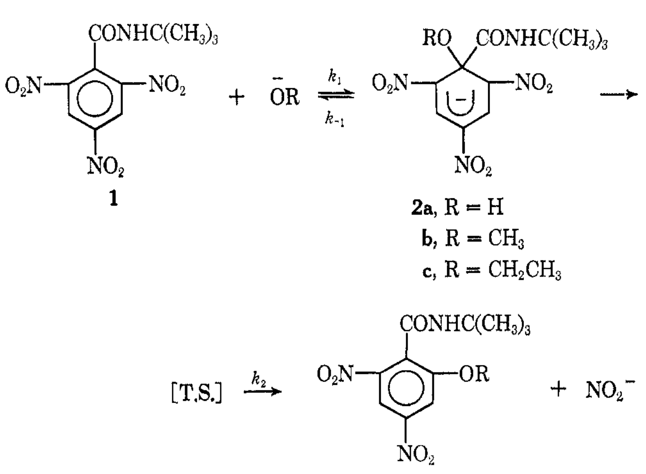
The interaction of hydroxide and methoxide ions with *N-tert*-butyl-2,4,6-trinitrobenzamide (**1**) in water and in methanol, respectively, results in the equilibrium formation of the 1-OH- (or -OCH_3-) 1-$CONHC(CH_3)_3$-2,4,6-$(NO_2)_3C_6H_2$ Meisenheimer complex and the formation of nitrite ions. Rate constants for the formation, k_1, and decomposition, k_{-1}, of these complexes as well as those for nitrite ion production, k_2, have been determined. At 25.00° for hydroxide ion interaction with **1** in water, $k_1 = 17.6$ l. mol^{-1} sec^{-1}, $k_{-1} = 0.0156$ sec^{-1}, and $k_2 = 1.43 \times 10^{-5}$ sec^{-1}, and for the methoxide ion interaction with **1** in methanol, $k_1 = 1.13 \times 10^3$ l. mol$^-$ sec^{-1}, $k_{-1} = 0.46$ sec^{-1}, and $k_2 = 6.7 \times 10^{-5}$ sec^{-1}. Equilibrium constants ($K = k_1/k_{-1}$) have been determined from kinetic measurements of the attainment of equilibrium for complex formation, from those of nitrite ion elimination, and from linear Benesi–Hildebrand plots. Excellent agreement among the three independently determined K values has been found. Structures of the hydroxy, methoxy, and ethoxy Meisenheimer complexes of **1** have been substantiated by pmr measurements of the isolated and *in situ* generated complexes.

N-tert-Butyl-2,4,6-trinitrobenzamide (**1**) was reported to undergo nucleophilic substitution with "hydroxide ion" in aqueous methanol (50/50 v/v) producing nitrite ions.[4] The formation of a red color upon the addition of the base to **1** led to the postulation of the presence of a complex.[4] The nature of these experiments, however, precluded the quantitative assessment of all the kinetic steps involved. The replacement of a nitro group on the aromatic ring by lyate ions as well as the relative steric, inductive, and resonance effects of the *tert*-butylamido group on the equilibrium constant for complex formation render the detailed kinetic investigation of this system particularly important. We have obtained data for the attainment of the equilibrium for the formation of the hydroxy and methoxy adducts of **1**, in pure water and in pure methanol, respectively, and for the formation of nitrite ions at different lyate ion concentrations. Using these data the rate constants k_1, k_{-1}, and k_2 in



have been obtained. Additionally we have elucidated the structures of **2a**, **2b**, and **2c** using proton magnetic resonance spectroscopy both for the isolated and the *in situ* generated complexes.

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[1] Part VIII: J. H. Fendler and E. J. Fendler, *J. Org. Chem.*, **35**, 3378 (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. Buncel, 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] Address inquiries to Department of Chemistry, Texas A & M University, College Station, Texas 77843.

[4] P. J. Hutchinson and R. S. L. Martin, *Aust. J. Chem.*, **18**, 699 (1965).

Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.[5] *N,N*-Dimethylacetamide (DMA, Baker analyzed reagent grade) was stored over Linde Type 5A Molecular Sieve and it spurity was verified by its pmr spectrum. The pH of the buffer solutions was measured at 25.00° either with an Orion-801 or a Radiometer PHM 26 pH meter.

2,4,6-Trinitrobenzoyl chloride was prepared, according to a slightly modified procedure of Hutchison and Martin,[4] by the portionwise addition of 10 g of 2,4,6-trinitrobenzoic acid to a refluxing solution of thionyl chloride (50 ml) and dry benzene (50 ml) over a period of 8 hr. The reaction mixture was refluxed for *ca.* 12 hr, cooled, and rotary evaporated *in vacuo* to dryness. Benzene (100 ml) was mixed with the product and then removed with a vacuum rotary evaporator. After recrystallization from benzene–petroleum ether (bp 40–60°), the product melted at 162–163° (lit.[4] 156–157°).

Compound **1** was prepared from 2,4,6-trinitrobenzoyl chloride and *tert*-butylamine in benzene according to the procedure of Hutchison and Martin.[4] After two elutions through a column of neutral alumina with benzene–methanol (9/1, v/v) followed by recrystallization from benzene–petroleum ether (bp 40–60°), the white crystals melted at 244–244.5° (lit.[4] mp 234–235°).

The **hydroxy complex (2a)** of ***N-tert*-butyl-2,4,6-trinitrobenzamide** was prepared by the addition of 0.25 ml (0.5 mmol) of 2.00 *M* aqueous potassium hydroxide (BDH) to a warm solution of 0.1495 g (0.5 mmol) of **1** in 0.90 ml of dioxane. The dark red crystals which appeared after *ca.* 2 min were removed by filtration under dry nitrogen and were washed with dry benzene and anhydrous ether. After drying *in vacuo* over phosphorus pentoxide, the crystalline product contained approximately 0.5 mol of dioxane of crystallization (by pmr integration of the dioxane singlet, τ 6.43).

Anal.[6] Calcd for $C_{11}H_{13}N_4O_8K \cdot 0.5C_4H_8O_2$: C, 37.9; H 4.16; N, 13.6; K, 9.50. Found: C, 37.24; H, 4.17; N, 13.01; K, 9.50.

The **methoxy complex (2b)** of ***N-tert*-butyl-2,4,6-trinitrobenzamide** was prepared analogously by the addition of 0.099 ml (0.5 mmol) of 5.05 *M* potassium methoxide in methanol to a warm solution of 0.1495 g (0.5 mmol) of **1** in 0.90 ml of dioxane under dry nitrogen. After filtration, washing, and drying, the fine red crystalline material was found to contain approximately 0.3 mol of dioxane of crystallization (pmr integration).

Anal.[6] Calcd for $C_{12}H_{15}N_4O_8K \cdot 0.3C_4H_8O_2$: C, 38.7; H, 4.28; N, 13.7; K, 9.55. Found: C, 35.26; H, 3.83; N, 13.22; K, 10.04.[7]

The same procedure was used to prepare the **ethoxy complex (2c)** of ***N-tert*-butyl-2,4,6-trinitrobenzamide** from 0.1495 g (0.5 mmol) of **1** in *ca.* 2.9 ml of dioxane and 0.207 ml (0.5 mmol) of 2.42 *M* potassium ethoxide in ethanol. The dark red product contained approximately 0.5 mol of dioxane of crystallization (pmr integration).

Anal.[6] Calcd for $C_{13}H_{17}N_4O_8 \cdot 0.5C_4H_8O_2$: C, 40.8; H, 4.82; N, 12.7; K, 8.90. Found: C, 38.14; H, 4.41; N, 12.71; K, 9.10.[7]

The attainment of the equilibria for the formation of **2a** in water was followed at 430 nm in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The temperature was measured inside the cells and was maintained within ±0.02°. The mixing techniques for fast reactions have been described previously.[10] Since the concentration of **1** was kept well below that of the hydroxide ion, good pseudo-first-order kinetics were observed for the attainment of the equilibrium for the formation of **2a**. The decomposition of solid **2b** was initiated by injecting a freshly prepared concentrated solution of **2b** in dioxane–methanol (50/50 v/v) into a thermostated solution of methanol. In all cases the final concentration of dioxane was 1 vol %. An increase in the dioxane concentration to 2 vol % had no observable effect on the rate constants.

Nitrite determinations were carried out on neutralized samples using the method of Rider and Mellon.[11] Good pseudo-first-order rate constants were obtained for the rate of nitrite appearance.

The 60-MHz pmr spectra were obtained with a Varian Associates A-60 spectrometer at ambient probe temperature, 31°. 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 (τ 10.00 ppm) and are accurate to ±0.03 ppm. Chemical shift data were taken from spectra determined at sweep widths of 500 Hz.

Results

In neutral aqueous buffered solution (pH 7.23), the absorption of *N-tert*-butyl-2,4,6-trinitrobenzamide (**1**) above 300 nm is negligible. At higher hydroxide ion concentrations (pH >9.0) a new absorption band, with a maximum at 430 nm, appears. This absorbance remains essentially constant over more than a decade of change in hydroxide ion concentration indicating the completion of the equilibrium (eq 1). In the concentration range of (2.5–27.5)10^{-4} *M* hydroxide ion and 3 × 10^{-5} *M* **1**, it was possible to follow the equilibrium attainment of **2a** by measuring the increase in the absorbance at 430 nm [ϵ_{430} for **2a** (2.5 ± 0.1)10^4 cm^{-1} l. mol^{-1}] as a function of time. Under the experimental conditions, the observed first-order rate constant for the attainment of equilibrium, k_{obsd}, is given by

$$1 + [OH^-] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{2a} \qquad (1)$$

$$k_{obsd} = k_1[OH^-] + k_{-1} \qquad (2)$$

where k_1 is the second-order rate constant for the formation of **2a** and k_{-1} is the first-order rate constant for its decomposition.[1,9,10] Table I contains the data for the attainment of equilibrium for the formation of **2a** at 15.20 and 25.00° at different hydroxide ion concentrations. Good linear plots of k_{obsd} *vs.* [OH$^-$] were obtained at both temperatures from which values for

Table I

Interaction of *N-tert*-Butyl-2,4,6-trinitrobenzamide (1) (*ca.* 3 × 10^{-5} *M*) with Hydroxide Ion in Aqueous Solution

Temp, °C	10^4[OH$^-$], *M*[a]	10^2k_{obsd}, sec^{-1}	k_1, M^{-1} sec^{-1} [b]	10^2k_{-1}, sec^{-1} [c]
15.20	0.00		9.20	0.57
	2.50	0.75		
	4.30	0.85		
	4.90	0.94		
	10.50	1.25		
	17.30	1.75		
	20.20	2.00		
	26.90	2.40		
	35.40	3.01		
25.00	0.00		17.6	1.56
	4.30	2.37		
	6.30	2.65		
	8.40	3.05		
	14.90	4.25		
	17.70	4.70		
	27.50	6.35		

[a] 1.0 × 10^{-2} *M* $Na_2B_4O_7$ or Na_2HPO_4 buffers. [b] Obtained from the slope of k_{obsd} *vs.* [OH$^-$], *M*. [c] Obtained from the intercept of the plot of k_{obsd} *vs.* [OH$^-$], *M*.

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

[6] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[7] As in the case of other crystalline Meisenheimer complexes,[1,8,9] the carbon and hydrogen analyses are low possibly due to the loss of methanol or ethanol during analysis or the presence of carbonate in the ash.

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

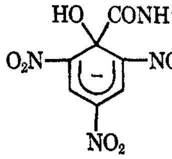
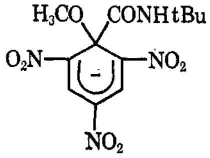
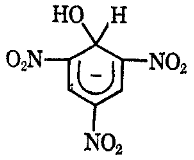
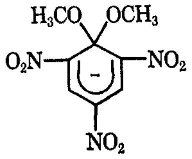
[9] E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larsen, *J. Org. Chem.*, **35**, 287 (1970).

[10] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *ibid.*, **34**, 689 (1969).

[11] B. F. Rider and M. G. Mellon, *Anal. Chem.*, **18**, 96 (1946).

TABLE II

KINETIC AND THERMODYNAMIC PARAMETERS FOR MEISENHEIMER COMPLEXES AT 25.00°

	 **2a** in H_2O	 **2b** in MeOH	 **3**[a] in H_2O	 **4**[b] in MeOH
k_1, l. mol^{-1} sec^{-1}	17.6	1.13×10^3 [c]	37.5	17.3
k_{-1}, sec^{-1}	0.0156	0.46	9.8	1.0×10^{-3}
K, l. mol^{-1}	1130[d] 1240[e] 1220[f]	548[e] 520[f]	3.7	17,000
$\Delta H_1^{\ddagger}$, kcal mol^{-1}	11.0 ± 1.0		15.6 ± 0.8	12.9 ± 1.0
$\Delta S_1^{\ddagger}$, eu	−15.6 ± 3.0		1.1 ± 2.7	−9.4 ± 3.4
$\Delta H_{-1}^{\ddagger}$, kcal mol^{-1}	19.4 ± 1.0		7.3 ± 0.8	18.4 ± 1.0
$\Delta S_{-1}^{\ddagger}$, eu	2.6 ± 3.0		−29.4 ± 2.7	−4.8 ± 3.4

[a] Reference 17. [b] Reference 10. [c] Estimated value; see Results. [d] Obtained from eq 2. [e] Obtained from eq 8. [f] Obtained from eq 3.

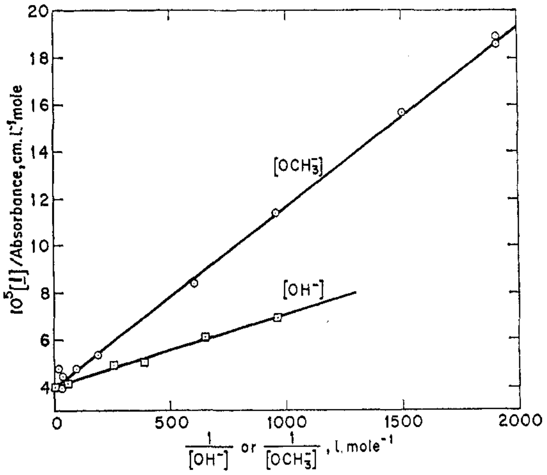


Figure 1.—Benesi-Hildebrand plots for the interaction of methoxide ion with 1 in methanol and for that of hydroxide ion with 1 in water at 25.00°.

k_1 and k_{-1} were calculated and are also given in Table I. Enthalpies and entropies of activation of these processes are given in Table II.

As the hydroxide ion concentration is increased above 10^{-1} M, the absorbance increases somewhat and the absorption band exhibits a bathochromic shift until it reaches 450 nm at 1.0 M NaOH.

The absorption spectra of 1 in methanol is similar to that in water, and in methanolic methoxide solutions it resembles that in aqueous solutions of sodium hydroxide with an absorption maximum at 430 nm.

Using the obtained absolute absorbances and the Benesi-Hildebrand equation[12]

$$\frac{[1]}{A} = \frac{1}{\epsilon} + \frac{1}{K\epsilon([OH^-] \text{ or } [OCH_3^-])} \qquad (3)$$

where A is the absorbance in a 1.0-cm cell, ϵ is the molar extinction coefficient, and K is the equilibrium constant ($K = k_1/k_{-1}$), good linear relationships were obtained on plotting $[1]/A$ against $1/[OH^-]$ or $1/[OCH_3^-]$ (Figure 1). The obtained equilibrium constants are given in Table II.

Attempts to follow the attainment of the equilibrium for the formation of **2b** were unsuccessful. Even at the lowest methoxide ion concentration the reaction was found to be too rapid to measure by our techniques. The equilibrium constant could be obtained, however, by the use of eq 3 (Table II). The decomposition of isolated solid **2b** in methanol at 25.00° gave k_{-1} = 0.46 sec^{-1} (mean of three determinations) which, with the value of $K_{OCH_3^-}$ = 520 l. mol^{-1} sec^{-1}, allows the estimation of k_1 to be 1.13×10^3 l. mol^{-1} sec^{-1}.

The observed first-order rate constants for the appearance of nitrite ion, $k_\psi^{NO_2^-}$, in methanol and in water are given in Table III. At infinity time the amount of nitrite ion formed ranged from 60 to 90% with respect to 1.

TABLE III

PSEUDO-FIRST-ORDER CONSTANTS FOR THE APPEARANCE OF NITRITE ION ($k_\psi^{NO_2^-}$) AT 25.00° [a]

$10^4[NaOCH_3]$, M	$10^6 k_\psi^{NO_2^-}$, sec^{-1}
In Methanol	
5.30	1.49
8.82	2.30
10.64	2.61
17.60	3.22
35.20	4.44
48.90	4.16
88.20	5.75
In Water	
$10^4[OH^-]$, M	$10^6 k_\psi^{NO_2^-}$, sec^{-1}
0.637[b]	1.03
1.45[b]	2.25
2.35[b]	2.93
4.58[b]	6.19
123.0[c]	14.20

[a] [1] ≃ 4×10^{-5} M. [b] 1.0×10^{-2} M $Na_2B_4O_7$ buffer. [c] 1.0×10^{-2} Na_2HPO_4 buffer.

The amide 1 has been shown to be stable to hydrolysis under the conditions used in these experiments and the product of the reaction of methoxide ions with 1 was previously established to be *N-tert*-butyl-2-methoxy-4,6-dinitrobenzamide.[4]

The pmr parameters for 1, **2a**, **2b**, and **2c** are collected in Table IV.

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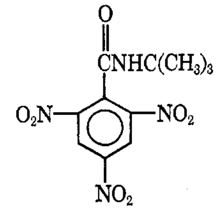
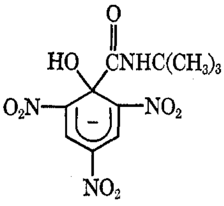
[12] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

TABLE IV

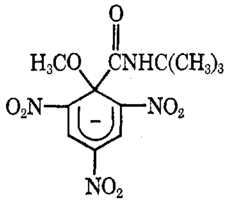
PMR SPECTRA OF *N-tert*-BUTYL-2,4,6-TRINITROBENZAMIDE AND ITS MEISENHEIMER COMPLEXES



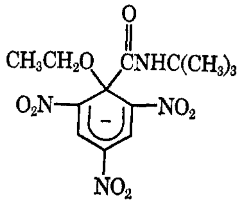
1



2a



2b[a]



2c

	1		2a	2b[a]		2c
	DMSO-d_6	DMA	DMSO-d_6	DMSO-d_6	DMA	DMSO-d_6
$\tau_{C(CH_3)_3}$	8.65	8.59	8.71	8.72 (8.72)	(8.60)	8.71
τ_{NH}	1.28	1.19	2.82	3.10	(3.12)	3.06
$\tau_{H\text{-}3,H\text{-}}$	0.93	0.83	1.55	1.38 (1.36)	(1.28)	1.39
τ_{OCH_3}				7.13 (7.13)		
τ_{OH}			3.62			
$\tau_{OCH_2CH_3}$[b]						6.98
$\tau_{OCH_2CH_3}$[c]						8.98

[a] Values in parenthesis have been obtained in the *in situ* generation of **2b** by the dropwise addition of 5.05 *M* potassium methoxide in methanol to a solution of **1** in the indicated solvent. [b] OCH_2CH_3. [c] OCH_2CH_3.

Discussion

The interaction of hydroxide ion with *N-tert*-butyl-2,4,6-trinitrobenzamide (**1**) in aqueous solution results in the equilibrium formation of the hydroxyl adduct of **1** (**2a**). The structure of this adduct has been inferred from its absorption spectra and has been established unequivocally from the proton magnetic resonance spectra of the *in situ* generated and isolated complexes **2a** (*vide infra*) and elemental analysis of the isolated complex **2a**. It is of interest to consider the requirements for Meisenheimer complex formation in aqueous solutions. No detectable complex formation has been observed in the interaction of hydroxide ions with several picryl alkyl and aryl ethers,[13] picryl chloride,[13] and picryl fluoride[13] or with 1,2,4,5-tetranitrobenzene[14] in aqueous solutions. 1,3,5-Tri-[15] and 1,2,3,5-tetranitrobenzene[14] and 1-(β-hydroxyethoxy)-2,4,6-trinitrobenzene,[16] on the other hand, readily form cyclohexadienylide ions, Meisenheimer complexes, in aqueous solutions with equilibrium constants in the range of 3–10^5 l. mol^{-1}.[16] It appears, therefore, that steric factors in addition to inductive and resonance contributions affect the position of initial attack as well as the stability of the transient intermediate complex.

The observed pseudo-first-order rate constant for nitrite ion appearance is

$$k_\psi^{NO_2^-} = k_2[\mathbf{2a}] \tag{4}$$

At time t the total amount of **1** is given by

$$[\mathbf{1}]_{total} = [\mathbf{1}]_{free} + [\mathbf{2a}] \tag{5}$$

and the equilibrium constant for complex formation is expressed as

$$K = \frac{[\mathbf{2a}]}{([\mathbf{1}]_{total} - [\mathbf{2a}])[OR^-]} \tag{6}$$

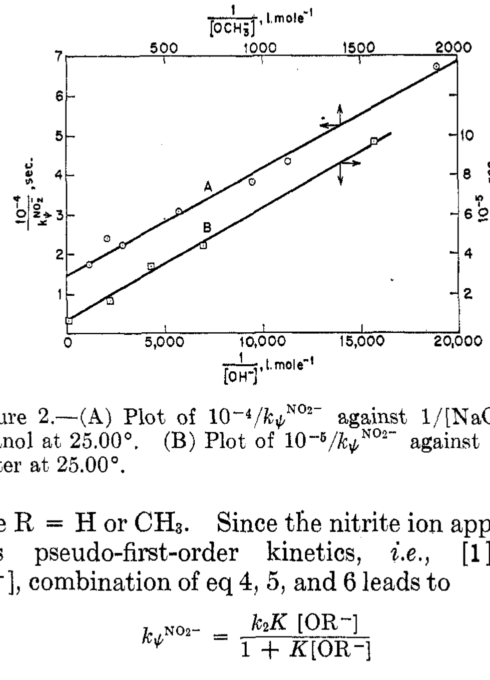


Figure 2.—(A) Plot of $10^{-4}/k_\psi^{NO_2^-}$ against 1/[NaOCH$_3$] in methanol at 25.00°. (B) Plot of $10^{-5}/k_\psi^{NO_2^-}$ against 1/[OH$^-$] in water at 25.00°.

where R = H or CH$_3$. Since the nitrite ion appearance obeys pseudo-first-order kinetics, *i.e.*, $[\mathbf{1}]_{total} < [OR^-]$, combination of eq 4, 5, and 6 leads to

$$k_\psi^{NO_2^-} = \frac{k_2K\,[OR^-]}{1 + K[OR^-]} \tag{7}$$

Inversion of eq 7 gives

$$\frac{1}{k_\psi^{NO_2^-}} = \frac{1}{k_2} + \frac{1}{k_2K}\,\frac{1}{[OR^-]} \tag{8}$$

according to which a plot of $1/k_\psi^{NO_2^-}$ *vs.* 1/[OR$^-$] should give a straight line whose slope is $1/k_2K$ and intercept is $1/k_2$. The observed linear relationships (Figure 2) support the postulated mechanism and indicate, not unexpectedly, that the liberated nitrite ions do not participate in the formation of complex **2a**. From the intercept of the plot for the hydroxide ion reaction (Figure 2), k_2 has been calculated to be 1.43 × 10^{-5} sec^{-1}. From this value and the slope of the plot (eq 8 and Figure 2), *K* has been calculated to be 1240 l. mol^{-1} (Table II). The excellent agreement among the three independently determined equilibrium constants is very gratifying.

Qualitatively, the reaction of methoxide ion with **1** is similar to that of hydroxide ion in that the equilibrium

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(13) J. Murto, *Acta Chem. Scand.*, **20**, 310 (1966).

(14) M. R. Crampton and M. El Ghariani, *J. Chem. Soc. B*, 391 (1970).

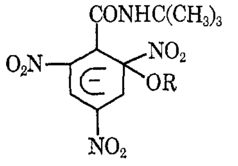
(15) V. Gold and C. Rochester, *J. Chem. Soc.*, 1710 (1964).

(16) J. Murto, *Suom. Kemistilehti B*, **38**, 255 (1965).

formation of a complex is followed by nitrite ion elimination. Furthermore, eq 8 is obeyed quantitatively (Figure 2) and the equilibrium constant obtained from it agrees well with that determined by means of the Benesi–Hildebrand equation (Table II). Not unexpectedly, however, there are significant quantitative differences between the reactivities of the two lyate ions in water and in methanol. While the equilibrium constant for the formation of **2b** is only a factor of 2 smaller than that for **2a**, the rate constant for complex formation (k_1) is a factor of 100 greater for the former than for the latter.

It is instructive to compare the kinetic and thermodynamic parameters for **2a** and **2b** with those obtained for the hydroxy complex of 1,3,5-trinitrobenzene (**3**)[17] and for the methoxyl complex of 2,4,6-trinitroanisole (**4**)[10] (Table II). The 300-fold greater value for K_{2a} relative to K_3 is reflected mainly in the difference between their decomposition rates, k_{-1} for **2a**/k_{-1} for **3** = 65 whereas k_1 for **2a**/k_1 for **3** = 0.47, suggesting that the stability of **2a** is primarily the consequence of the greater relief of steric strain by rehydridization of C-1 from sp^2 to sp^3 in the case of **2a**. The low enthalpy of activation required for the formation of **2a**, $\Delta H_1^{\ddagger}$, is contrasted with the considerable energy required for its decomposition, $\Delta H_{-1}^{\ddagger}$ (Table II). Both steric and solvation effects must contribute to the extremely rapid formation and fast decomposition of **2b**; however, the data does not allow a quantitative comparison of the activation parameters for **2b** and **4** at the present time.

The production of nitrite ions from **1** and lyate ions most probably involves a species such as **5**. Structures similar to **5** have been postulated in the interaction of lyate ions with 1,3,5-trinitrobenzene,[15] 3,5-dinitrobenzonitrile,[18] and 1,2,3,5- and 1,2,4,5-tetranitrobenzenes.[14] No nmr or spectrophotometric evidence has been obtained for the accumulation of **5**. **5** is, therefore, unlikely to be an intermediate but rather a transition state through which the products are formed. The rate-determining step in the liberation of nitrite ion is the formation of complex **5**, or a related structure, which rapidly loses nitrite ion. An analogous mechanism has been suggested for the reaction of hydroxide ion with 1,3,5-trinitrobenzene[15] and 1,2,3,5- and 1,2,4,5-tetranitrobenzene.[14] Lack of detection of **5** by usual kinetic and pmr spectroscopic techniques substantiates this postulation.



5

The rate constant for the formation of nitrite ions, k_2, has been calculated to be 1.43×10^{-5} sec^{-1} and 6.7×10^{-5} sec^{-1} for **2a** and **2b**, respectively. The rate constant for product formation from **3**[19] has been found to be some three orders of magnitude greater than those for **2a** and **2b**. These data, once again, reflect the differences in the equilibrium constants for the formation of **2a**, **2b**, and **3**.

We continue to use proton magnetic spectroscopic techniques to confirm the postulated structure of complexes **2a**, **2b**, and **2c** and to investigate the existence of other transient intermediates. No pmr data has previously been reported for Meisenheimer complexes of benzamides or other amido-substituted aromatic compounds.

The pmr parameters for the isolated complexes **2a**, **2b**, and **2c** (Table IV) are completely consistent with the postulated structures, *i.e.*, 1,1 complexes, and eliminate the possibility of alternative complexes such as those arising from attack at C-3, abstraction of the amido proton, or charge–transfer interactions. The pmr criteria for the structure of Meisenheimer complexes have been discussed previously[1,2,5,9,10,20] and therefore are not reiterated here in detail. Rehybridization of C-1 from sp^2 in **1** to sp^3 in **2a**, **2b**, and **2c** results in an upfield shift of the aromatic resonances ($\Delta\delta$ 0.62, 0.45, and 0.46 ppm, respectively) comparable to those found for 2,4,6-trinitroanisole[10] ($\Delta\delta$ 0.40), 4-cyano-2,6-dinitroanisole[10] ($\Delta\delta$ 0.65), 2,6-dicyano-4-nitroanisole[9] ($\Delta\delta$ 1.10), and diethyl 2,4,6-tricyanophenylphosphonate[21] ($\Delta\delta$ 0.38). The amido proton is also strongly shielded in complexes **2a**, **2b**, and **2c** relative to the parent benzamide **1** ($\Delta\delta$ 1.54–1.82) primarily reflecting the increase in charge density in the π system.

In the case of several activated aromatic systems, initial attack of the nucleophile has been found to occur at C-3 forming a thermodynamically unstable 1,3 complex.[1,2,9,10,22] In order to investigate the existence of any fairly stable transients in the interaction of methoxide ions with **1**, we examined the formation of **2b** *in situ* in DMSO-d_6 and DMA. In both solvents[23] no additional resonances were observed and, therefore, on the time scale necessitated by pmr techniques,[1,9,10] the 1,3 complex of **1** or other transients are either not formed or are not detectable.

Registry No.—**1**, 3099-54-5; **2a**, 28433-52-5; **2b**, 28433-53-6; **2c**, 28433-54-7.

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[23] DMA has been found to appreciably enhance the stabilities of 1,3-dimethoxycyclohexadienylide ions as compared to those in DMSO.[24]

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