

334. *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part V.¹ Solutions of Methyl Picrate and 1,3,5-Trinitrobenzene in Aqueous Sodium Hydroxide in the Absence of Light.*

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Methyl picrate reacts with weakly alkaline phosphate buffers with formation of the picrate ion. The kinetics are consistent with the interpretation that the rate-determining step is the attachment of a hydroxide group to the carbon atom to which the methoxyl group is attached. The rate of this reaction is *ca.* 4 times slower than the corresponding attachment of a methoxide group in methanol solution.

The formation of complexes from solutions of 1,3,5-trinitrobenzene and sodium hydroxide has been re-investigated. The equilibrium constant of formation of the 1:1 complex is in satisfactory agreement with earlier spectrophotometric determinations but disagrees with a reported polarographic determination. It is suggested that transitions to two different excited states are responsible for the broad absorption maximum of the 1:1 complex about 4500 Å. The formation of higher complexes (1:2?) in more concentrated sodium hydroxide is briefly investigated.

The irreversible further reaction of dilute solutions of trinitrobenzene with sodium hydroxide is shown to lead to substantial amounts of nitrite and ammonia, the yield of which decreases with increasing alkali concentration.

THE present and succeeding three Parts deal with the action of aqueous sodium hydroxide on 1,3,5-trinitrobenzene derivatives, the reactions of which have already been studied in methanolic sodium methoxide. For nearly all solutes unexpectedly large changes in

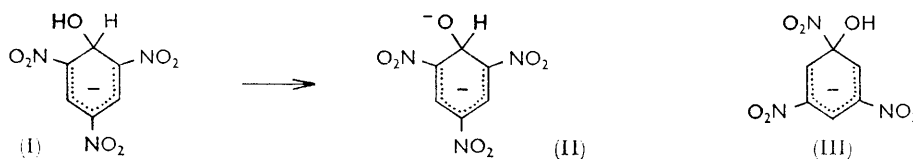
¹ Part IV, preceding paper.

behaviour are brought about by this change in the solvent system. The two compounds discussed in this Paper are least unusual in this respect. It was expected² that methyl picrate, for which the replacement of the methoxide group leads to no net chemical change in the methanol system, would undergo hydrolysis in an aqueous alkaline medium. The reaction of trinitrobenzene with sodium hydroxide is less clean than that with sodium methoxide and the products include 3,5,3',5'-tetranitroazoxybenzene and some 3,5-dinitrophenol.² Other side-reactions are less important when sodium hydroxide is replaced by sodium carbonate.³ It is not known with certainty to what extent the decreased alkalinity of the medium is responsible for this change.

The reversible colour changes which occur before irreversibly formed products appear have been held to indicate the formation of a coloured 1 : 1 complex at low (<0.5N) concentrations of sodium hydroxide and a colourless 1 : 2 complex in more alkaline solution.^{4,5} The equilibrium constant for formation of the 1 : 1 complex A from trinitrobenzene, *i.e.*, $K_A = [A]/[\text{TNB}][\text{OH}^-]$, derived from these measurements⁵ at 25°, is 2.7 l. mole⁻¹. Earlier spectroscopic measurements had given values of *ca.* 1.5 (ref. 4), 3.6—6.7 (ref. 6a), and *ca.* 3 (ref. 6b). An earlier polarographic investigation^{6c} led to a value of 347 l. mole⁻¹ for K_A , and, in addition, to constants for higher (1 : 2, B; 1 : 3, C) complexes, namely,

$$K_B = [B]/[A][\text{OH}^-] = 18.2, \text{ and } K_C = [C]/[B][\text{OH}^-] = 2.5 \text{ l. mole}^{-1}.$$

The structures of these complexes present problems similar to those with the methoxide complexes, with the added possibility that a 1 : 2 complex may represent proton loss from



the hydroxyl group of a 1 : 1 complex formed by addition, *i.e.*, (I) \longrightarrow (II). To account for the formation of 3,5-dinitrophenol among the products of the reaction between trinitrobenzene and aqueous sodium hydroxide, Abe has proposed that the red colour must be due at least in part to the structure (III).⁷ The argument is probably overstated, in that the nature of the product does not require a detectable *equilibrium* concentration of a structure of this type, although it is highly probable that such a configuration would be passed through.

The present study, which is confined to processes which occur in the absence of photochemical reactions,⁸ deals with the kinetics of the hydrolysis of methyl picrate, the equilibria of trinitrobenzene, and certain aspects of the thermal reactions of that compound.

EXPERIMENTAL

The purification of organic materials, and other general procedures, have been described.⁹ Aqueous sodium hydroxide solutions were made from AnalaR pellets which had been rinsed with distilled water and quickly dissolved in fresh distilled water. The concentration was determined by titrimetric reference to anhydrous sodium carbonate (*via* hydrochloric acid).

² Cahours, *Ann. Chim.*, 1849, [3], 25, 26.

³ Lobry de Bruyn and van Leent, *Rec. Trav. chim.*, 1894, 13, 148.

⁴ Čiža and Písecký, *Chem. listy*, 1957, 51, 433; *Coll. Czech. Chem. Comm.*, 1958, 23, 628.

⁵ Abe, *Bull. Chem. Soc. Japan*, 1960, 33, 41.

⁶ (a) Eisenbrand and Halban, *Z. phys. Chem.*, 1930, A, 146, 11; (b) Salm, *ibid.*, 1907, 57, 471; (c) Holleck and Perret, *Z. Elektrochem.*, 1955, 59, 114.

⁷ Abe, *Bull. Chem. Soc. Japan*, 1959, 32, 339, 997.

⁸ Gold and Rochester, *Proc. Chem. Soc.*, 1960, 403.

⁹ Gold and Rochester: (a) Part I, *J.*, 1964, 1687; (b) Part II, *J.*, 1964, 1692.

Nitrite estimations were carried out by Rider and Mellon's method.¹⁰ Ammonia analyses were performed by spectrophotometry of the blue solutions obtained by addition of phenol-hypochlorite reagent.^{11,12} Both techniques for ammonia estimation were standardized against AnalaR ammonium nitrate.

Methyl Picrate.—The velocity of hydrolysis in dilute phosphate buffers¹³ at 25° was followed by spectrophotometric observation (at 3600 Å) of the formation of the picrate ion. The spectrum of a solution of methyl picrate (4.96×10^{-5} M) in 0.223M-sodium hydroxide, recorded less than 15 min. after preparation, was identical with that of picric acid in a solution of the same hydroxide concentration. No intermediate colour change is observed during the course of slow hydrolysis, which exactly obeys a first-order rate law (Table 1). The value of $k/\text{antilog}(-\text{pOH})$ is 1.2_4 l. mole⁻¹ sec.⁻¹. This will differ from the second-order constant $k' = k/[\text{OH}^-]$ to the extent of an (almost constant) activity coefficient factor. This factor will make k' of the order of 30% less than 1.2_4 l. mole⁻¹ sec.⁻¹ but is probably not known as precisely as the other parameters involved.

TABLE 1.

Hydrolysis of methyl picrate.					
Expt.	Buffer compn. (x) *	pH †	10^4 antilog ($-\text{pOH}$) ‡	$10^4 k$ (sec. ⁻¹)	k' §
1	3	10.86 ₀	7.3	7.0 ₆	0.97
2	5	11.09 ₁	12.4	15.0	1.21
3	10	11.44 ₅	28.0	32.4	1.16
4	15	11.65 ₇	45.7	60.4	1.32
5	20	11.82 ₁	66.7	83.3	1.25

* Buffer solutions were prepared by diluting 50 ml. of 0.05M-aqueous disodium hydrogen phosphate + x ml. of 0.1M-aqueous sodium hydroxide to 100 ml. † Interpolated from Table in ref. 13. ‡ $-\text{pOH} = \text{pH} - 13.997$. § $k' = k/\text{antilog}(-\text{pOH})$.

1,3,5-Trinitrobenzene.—The spectrum of a solution of trinitrobenzene in 0.415M-sodium hydroxide, recorded within 2 hr. of preparation, had a shape in substantial agreement with previous reports.^{4,5} At this concentration the solution fades slowly (half-life *ca.* 13 hr.). In order to compare the intensity of the initial colour at different concentrations of sodium

TABLE 2.

1,3,5-Trinitrobenzene. Variation of zero-time optical density at 4400 Å with concentration of sodium hydroxide ($[\text{TNB}]_{\text{stoich}} = 7.45 \times 10^{-5}$ M).

$[\text{OH}^-]$ (M)	D_0	$[\text{OH}^-]$	D_0	$[\text{OH}^-]$	D_0
0	0.000				
0.0195	0.113	0.0973	0.581	0.605	1.135
0.0389	0.242	0.1188	0.603	1.211	0.940
0.0584	0.352	0.178	0.806	1.816	0.730
0.0594	0.320	0.297	1.065	2.421	0.535
0.0778	0.470	0.416	1.140	3.027	0.360

hydroxide, measurements of optical density at 4400 Å as a function of time were used to determine the rate of fading, and hence an extrapolated value of the optical density at zero time (Table 2). Acidification of fresh solutions with aqueous hydrochloric acid regenerated trinitrobenzene (as indicated by the absorption spectrum).

Like Abe's results⁵ the initial optical densities point to the formation of at least two complexes, a situation reminiscent of the equilibria of *NN*-dimethylpicramide with sodium methoxide in methanol.¹⁴ In view of the steady decline of the absorption at high and increasing

¹⁰ Rider and Mellon, *Analyt. Chem.*, 1946, **18**, 96.

¹¹ Russell, *J. Biol. Chem.*, 1944, **156**, 457.

¹² Snell and Snell, "Colorimetric Methods of Analysis," Vol. II, van Nostrand, New York, 1949, p. 818.

¹³ Bates and Bower, *Analyt. Chem.*, 1956, **28**, 1322.

¹⁴ Part III, Gold and Rochester, *J.*, 1964, 1697.

hydroxide concentrations, we shall assume that the absorption of the higher complex is negligible at 4400 Å. If the equilibria are represented as



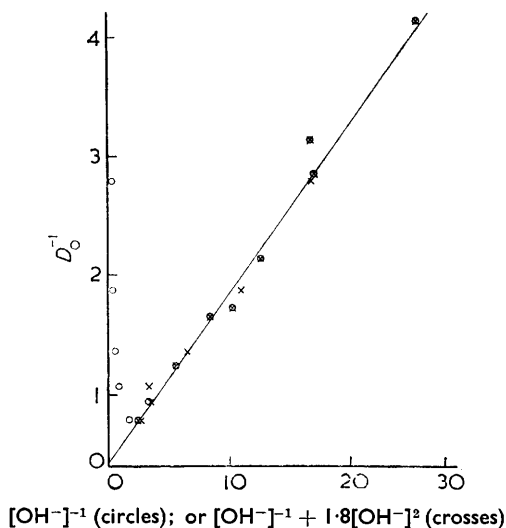
with $[\text{TNB}]_{\text{stoich}} = [\text{TNB}] + [\text{A}] + [\text{B}]$

we obtain, by steps analogous to those used in the derivation of eqn. (9) of Part III,¹⁴

$$\frac{1}{D_0} = \frac{1}{\epsilon_A [\text{TNB}]_{\text{stoich}} K_A} \left\{ \frac{1}{[\text{OH}^-]} + K_A K_n [\text{OH}^-]^n \right\} + \frac{1}{\epsilon_1 [\text{TNB}]_{\text{stoich}}} \quad (1)$$

When $K_A K_n [\text{OH}^-]^n \ll [\text{OH}^-]^{-1}$ this equation goes over into the Benesi-Hildebrand equation [see eqn. (4) of Part II¹⁶], and Abe has attempted to obtain values of K_A and ϵ_A from the linear portion of the Benesi-Hildebrand plot of D_0^{-1} against $[\text{OH}^-]^{-1}$ (where this simplifying condition would apply). Our corresponding plot is given in the Figure (circles). In practice the intercept is too small and uncertain for an accurate estimate of ϵ_A and K_A to be made, and thus Abe's values cannot be considered reliable.

Benesi-Hildebrand plot and test of eqn. (1) for 1,3,5-trinitrobenzene-sodium hydroxide in water at 28°.



If we make the assumption that ϵ_A is 30,000 (an estimate based on the maximum extinction coefficient of the 1:1 complex between trinitrobenzene and sodium methoxide, which is unlikely to be in error by more than a factor of two), K_A can be evaluated from the slope of the linear portion in the Figure alone, *i.e.*,

$$\text{Slope} = 1/(\epsilon_A [\text{TNB}]_{\text{stoich}} K_A) = 0.16,$$

whence $K_A = (0.16 \times 30,000 \times 7.8 \times 10^{-5})^{-1} = 2.7 \text{ l. mole}^{-1}$, which is the same as Abe's estimate of 2.7. However, we regard both these values to be accurate only within a factor of two, *i.e.*, much less certain than the closeness of the agreement might suggest. We find that a fairly linear graph is obtained over the entire concentration range when D_0^{-1} is plotted against $([\text{OH}^-]^{-1} + 1.8[\text{OH}^-]^2)$, corresponding to the values $n = 2$ and $K_n = 0.67 \text{ l.}^2 \text{ mole}^{-2}$ (crosses in the Figure). In view of the high concentration range of sodium hydroxide in which the squared term is significant, this particular form of law probably does not have a simple

significance. The complex B may therefore possibly arise from reaction of only one further hydroxide ion with A, the square dependence on the concentration being due to an activity coefficient effect (cf. Part III¹⁴).

The stoichiometry of the irreversible process is complex. The appearance of the final spectrum suggests that 3,5-dinitrophenol and picric acid are among the products, but these products together can account for less than half of the initial amount of trinitrobenzene. Simultaneous observations of the progress of the reaction by spectrophotometry (at 4400 Å), and nitrite estimation, gave discrepant results, the loss of colour being a more rapid reaction

TABLE 3.

Comparison of rates of fading and nitrite formation for trinitrobenzene in aqueous sodium hydroxide.

[NaOH] = 0.41M; [TNB]_{stoich} = 7.45 × 10⁻⁵M.

Time (hr.)	% reaction		Time (hr.)	% reaction		Time (hr.)	% reaction	
	Fading *	NO ₂ ⁻ formation †		Fading *	NO ₂ ⁻ formation †		Fading *	NO ₂ ⁻ formation †
0.82	2.7	—	14.69	—	33.4	25.13	—	
4.67	—	7.1	16.17	58.7	—	29.45	—	
5.17	19.4	—	19.77	—	42.7	30.98	84.9	
8.98	—	17.2	21.26	70.9	—	38.47	—	
9.37	37.0	—	24.35	—	55.5	38.97	90.4	

* Percentage of reaction = 100(D_t - D₀)/(D_∞ - D₀). † Percentage of reaction = 100[NO₂⁻]/[NO₂⁻]_∞.

TABLE 4.

Yields of inorganic products from reaction of trinitrobenzene.

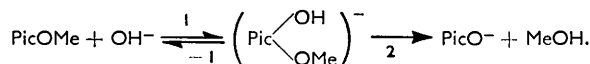
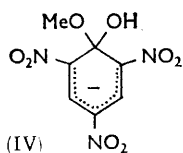
[TNB]_{stoich} = 7.45 × 10⁻⁵M for nitrite run; 3.55 × 10⁻⁵M for ammonia run.

[NaOH] (M)	100[NO ₂ ⁻]/[TNB] _{stoich}	100[NH ₃]/[TNB] _{stoich}	[NaOH] (M)	100[NO ₂ ⁻]/[TNB] _{stoich}	100[NH ₃]/[TNB] _{stoich}
0.195	73	—	1.175	—	16
0.409	72	—	1.635	49	—
0.588	—	19	1.763	—	14
0.818	64	—	2.433	42	—
1.168	55	—			

than the formation of nitrite (Table 3). It was shown in one case that the rate of fading was the same in sodium and potassium hydroxide solutions of equal concentration. Ammonia and nitrite analyses of final reaction mixtures confirmed that the former substance contributed a significant fraction of the inorganic nitrogen released,^{3,15} and showed that the yield of both these products decreased with increasing concentration of sodium hydroxide (Table 4).

DISCUSSION

The kinetic and thermodynamic results in the present Paper can be compared with those for the same substrates in methanolic sodium methoxide solution. The hydrolysis of methyl picrate occurs without evident formation of an intermediate sufficiently stable to accumulate during the reaction. It is likely that a configuration (IV) would be passed through, and the hydrolysis can be dissected into two steps, as commonly assumed for nucleophilic aromatic substitution reactions:¹⁶

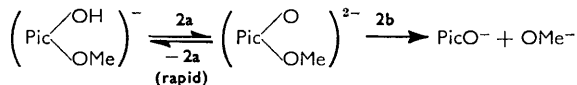


Reversibility of step 2 need not be considered, since the concentration of methoxide is

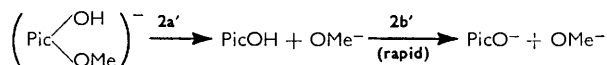
¹⁵ Ryan and O'Riordan, *Proc. Roy. Irish Acad.*, 1917/19, **34**, B, 180.

¹⁶ See, e.g., Bunnett, *Quart. Rev.*, 1958, **12**, 1.

negligible throughout. This reaction is probably composed of a sequence of steps, of which



and



are plausible alternatives. The details of reaction 2 are not important to the present argument. In view of the absence of a detectable concentration of intermediate, the velocity of hydrolysis can be expressed as:

$$d[\text{PicO}^-]/dt = \{k_1 k_2 / (k_{-1} + k_2)\} [\text{PicOMe}] [\text{OH}^-].$$

The ratio $k_2/(k_{-1} + k_2)$ is a measure of the relative leaving tendencies of methoxyl and hydroxyl groups. A similar problem has been analysed for the reaction between ethyl benzoate and hydroxide ions,¹⁷ where the alkoxide (ethoxide) group leaves considerably more easily [$k_{-1}/k_2 = 0.18$; $k_2/(k_{-1} + k_2) = 0.85$]. A reversal of this tendency is not expected in the present example, and accordingly the measured rate constant k' should be close in value to the rate constant k_1 ; k_1 is probably *ca.* 1.1–1.3 times k' so that k_1 is *ca.* 1 l. mole⁻¹ sec.⁻¹ (compared with a value of *ca.* 4 l. mole⁻¹ sec.⁻¹ for the attachment of methoxide ion to methyl picrate in methanol solution at the same temperature). This sequence of reactivities is in the same order as for the solvolyses of 4-chloro-3,5-dinitrobenzoate,¹⁸ where the reaction is expected similarly to be controlled by the initial addition of lyate ion. Since these two sets of rate comparisons involve both solvent and reagent change, the ratios observed are not a direct measure of the nucleophilicities of the two lyate ions.¹⁹

A comparison of the half-life of fading (Table 3) with the corresponding rate constant in the methanol system (Part II,^{9b} Table 2) suggests that the latter system is more reactive by a factor of about 20, but the comparison is approximate since the reaction does not take quite the same course in the two media.

The absorption spectrum of the 1:1 complex A shows a broad maximum whose appearance suggests that it is composed of two bands, as in the case of the methoxide complex, but with a small separation between the bands. It is suggestive to think of the spectrum of the hydroxide-complex as being produced from that of the methoxide complex by a shift towards longer wavelengths, and by a general broadening of the bands owing to stronger local interactions. The bathochromic shift is considered to be a solvent effect rather than a substituent effect, since the comparison of the spectra of trinitrobenzene and methyl picrate in methanolic sodium methoxide indicated that the spectra were not sensitive to substituent groups. A solvent effect in this direction would occur if the excited states were more polar in character than the ground state.²⁰ The kinetics of the photochemical methanolysis of trinitrobenzene suggest that irradiation of such alkaline solutions generates an excited state in which the negative charge is driven towards the periphery of the complex.¹ Such an excited state would be stabilized relative to the ground state by interaction with a more polar solvent. The energy of the optical transition would thus be lowered in the required sense. The appearance of the absorption spectrum is thus compatible with structure (I) for A, analogous to the methoxide complex.

¹⁷ Bender, Ginger, and Unik, *J. Amer. Chem. Soc.*, 1958, **76**, 3350.

¹⁸ Miller, *Chem. and Ind.*, 1953, 40.

¹⁹ Bunnett and Davis, *J. Amer. Chem. Soc.*, 1954, **76**, 3011.

²⁰ *E.g.*, Förster, *Z. Elektrochem.*, 1939, **45**, 548; Brooker, *J. Amer. Chem. Soc.*, 1951, **73**, 5332, 5350; Lippert, *Z. Elektrochem.*, 1957, **61**, 962; McRae, *J. Phys. Chem.*, 1957, **61**, 562.

1716 *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part V.*

The equilibrium constant for formation ($K_A = 2.7 \text{ l. mole}^{-1}$) differs from that in the methanol system (15 l. mole^{-1}) at the same temperature (28°) by a small factor. Our value for the hydroxide complex agrees with that obtained by Abe⁵ and confirms the substantial correctness of earlier values.^{4,6a,6b} We cannot account for the completely different results obtained by Holleck and Perret.^{6c}

The second complex (B), in which the ratio hydroxide : trinitrobenzene is greater than unity, is characterized by much lower light-absorption in the visible region, and in this respect it resembles *NN*-dimethylpicramide in methanolic sodium methoxide, but not methyl picrate in that solvent system. There is insufficient information to draw any convincing conclusion from these observations.

The difference in the course of the further reaction of trinitrobenzene in aqueous alkali from the reaction in methanol solution can be rationalized in terms of the foregoing measurements. It is evident that loss of a hydride ion instead of a hydroxide ion from structure (I) would lead to the formation of picric acid, the presence of which is indicated in the reaction products. The existence of the free hydride ion in these solutions is, of course, not required, but merely that (I) should be a reducing agent. This is confirmed by the ability of the solution to reduce potassium ferricyanide with rapid formation of picric acid.²¹ The reducing power of (I) is thus thought to be responsible for the formation of reduction products of trinitrobenzene, particularly 3,5,3',5'-tetranitroazoxybenzene,³ and of ammonia which would be formed by reduction of the nitrite ion. It has been suggested¹⁵ that one of the reduction products is 3,5-dinitroaniline which then reacts rapidly with alkali to liberate ammonia. This sequence of events is improbable on general grounds and also because Bader unsuccessfully investigated the possibility of preparing 3,5-dinitrophenol from 3,5-dinitroaniline.²² The fact that these side-reactions do not occur to the same extent in methanolic sodium methoxide is almost certainly a difference in degree rather than in kind. The simultaneous formation of a phenol and an azoxy-compound has been observed for several other aromatic nitro-compounds in alkaline solution,²³ and examples of other similar reductions have been cited by Sauer and Huisgen.²⁴ One difference between the hydroxide and methoxide solutions is the higher nucleophilic reactivity of methoxide in methanol compared with hydroxide in water; this would make the competing reactions less effective. However, it is not correct to look on the side-reaction as being principally due to bimolecular interaction of free trinitrobenzene and A. If this were so, the importance of the side-reaction should depend on the product of the concentrations of these two species. This is not borne out by the data in Table 4, and some additional factor, such as the reactivity of the second complex, must be invoked. If that complex were, for example, (II), which would be expected to be a stronger reducing agent than (I), then the decreasing importance of nitrite displacement with increasing alkali concentration might find an explanation.

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²¹ Hepp, *Annalen*, 1882, **215**, 345.

²² Bader, *Ber.*, 1891, **24**, 1653.

²³ Lobry de Bruyn, *Rec. Trav. chim.*, 1894, **13**, 101; 1901, **20**, 120.

²⁴ Wohl, *Ber.*, 1899, **32**, 3486; Aul, *Ber.*, 1901, **34**, 2442.

²⁵ Sauer and Huisgen, *Angew. Chem.*, 1960, **72**, 294.