

**336. Reactions of Aromatic Nitro-compounds in Alkaline Media. Part VII.<sup>1</sup> Behaviour of Picric Acid and of two Dihydroxydinitrobenzenes in Aqueous Sodium Hydroxide.**

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The indicator behaviour of picric acid in alkaline solution shows that the proportions of picrate ion and of a second complex, formed by further reaction with hydroxide ion, depend sensitively on the composition of the medium. The possible role of acidity functions ( $J_-$  and  $J_{2-}$ ) in equilibria of this type is briefly discussed. Alkaline solutions of picric acid react slowly to give nitrite, the formation of which is accelerated by visible light. It appears that both the picrate ion and the second complex undergo this photochemical reaction.

Absorption spectra of 3,5-dinitrocatechol and of 2,6-dinitroquinol in acid and in alkaline solution are given. The former substance is stable in alkaline solution, whereas the latter reacts, probably to form 2,6-dinitroquinone by the action of dissolved oxygen.

IN accordance with its high acid dissociation constant,<sup>2</sup> picric acid exists in dilute sodium hydroxide solution as the picrate ion. At concentrations of hydroxide ion greater than *ca.* 0.4M the spectrum of dilute solutions of the sodium picrate changes;<sup>3</sup> the absorption band with a maximum about 3600 Å disappears and is replaced by a more intense band having a maximum at 3900 Å. There is a fairly good isosbestic point<sup>3b</sup> between the two maxima, which suggests that the change is due to an equilibrium involving the reaction of picrate ion with hydroxide with formation of a single further species (with the reservation noted in Part III,<sup>4c</sup> p. 1703). The intensity of the absorption band at 3900 Å decreases with time.<sup>3b</sup> The present Paper examines this irreversible process, both in the presence and absence of light, and, in this connection, also the equilibrium between picrate ion and the "second complex" (the picrate ion being regarded as the "first" or 1:1 complex). As experimental results pointed to the possibility that 2,6-dinitroquinol and 3,5-dinitrocatechol might be among the products of hydrolytic reactions of picryl derivatives, a brief study of their behaviour in alkaline media has been included.

#### EXPERIMENTAL

Most details of procedures have already been described.<sup>4</sup> AnalaR picric acid was recrystallised from ether. 3,5-Dinitrocatechol was prepared from catechol which was first acetylated to give diacetylcatechol.<sup>5</sup> Nitration gave *OO*-diacetyl-3,5-dinitrocatechol,<sup>6</sup> and subsequent hydrolysis yielded 3,5-dinitrocatechol<sup>6</sup> (m. p., from ethanol, 164°; lit.,<sup>6</sup> 164°). 2,6-Dinitroquinol was obtained by benzylation of quinol, nitration (m. p. of 2,6-dinitrobenzoylquinol, 158.5°; lit.,<sup>6</sup> 151°), hydrolysis, and crystallisation from water,<sup>7</sup> m. p. 133°; lit.,<sup>7</sup> 134–135° (Found: C, 34.85; H, 2.7. Calc. for  $C_6H_4N_2O_6 \cdot H_2O$ : C, 33.0; H, 2.75%; for  $C_6H_4N_2O_6 \cdot \frac{1}{2}H_2O$ : C, 34.5; H, 2.4%; for  $C_6H_4N_2O_6 \cdot 1\frac{1}{2}H_2O$ , the formula deduced by Kehrmann *et al.*:<sup>7</sup> C, 31.7; H, 3.1%). Concentrations of the compound are based on the monohydrate formula.

The spectra of picric acid dissolved in water and in 7.95M-sodium hydroxide (Fig. 1) agree well with earlier spectra recorded over a shorter wavelength range.<sup>3b</sup> The intensity of the maximum at 3900 Å and the slow first-order disappearance of this band (at 40° for solutions protected from light) were recorded for a series of sodium hydroxide concentrations (Tables 1

<sup>1</sup> Part VI, preceding paper.

<sup>2</sup> von Halban and Seiler, *Helv. Chim. Acta*, 1938, **21**, 385.

<sup>3</sup> (a) Eisenbrand and von Halban, *Z. phys. Chem.*, 1930, **146**, 111; (b) Abe, *Nature*, 1960, **187**, 234.

<sup>4</sup> Gold and Rochester, *J.*, 1964, (a) Part I, p. 1687; (b) Part II, p. 1692; (c) Part III, p. 1697; (d) Part IV, p. 1704; (e) Part V, p. 1710.

<sup>5</sup> Nachbaur, *Annalen*, 1858, **107**, 243.

<sup>6</sup> Nietzki and Moll, *Ber.*, 1893, **26**, 2182.

<sup>7</sup> Kehrmann, Sandoz, and Monnier, *Helv. Chim. Acta*, 1921, **4**, 941.

and 2). Extinction coefficients at three other wavelengths for three different hydroxide concentrations are given in the second part of Table 1. The values of  $\alpha_1$  and  $\alpha_2$  represent the fractions of picric acid present in solution as the picrate ion and the second complex, respectively. They were calculated from the expressions  $\alpha_2 = (D_0 - 0.426)/0.425$ , and  $\alpha_1 = 1 - \alpha_2$  ( $D_0$  = initial optical density at 3900 Å), on the assumption that the only form present in the dilute aqueous solution is the picrate ion (in accordance with the reported acid dissociation constant <sup>2</sup>), and that only the second complex is present in 3.65M-sodium hydroxide (as suggested by the trend of the  $D_0$  values). The optical density at 3900 Å depends on a high

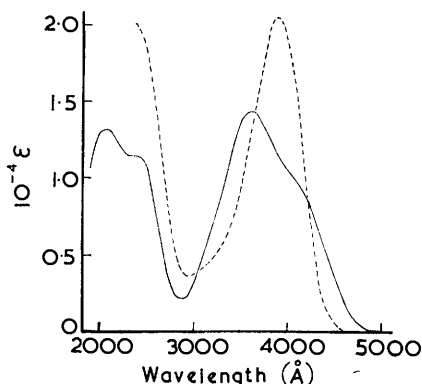


FIG. 1. Picric acid. Absorption spectra in water and 7.95M-sodium hydroxide.

Full line, water; broken line, 7.95M-sodium hydroxide.  $[P]_{\text{stoich}} = 4.07 \times 10^{-5}\text{M}$ .

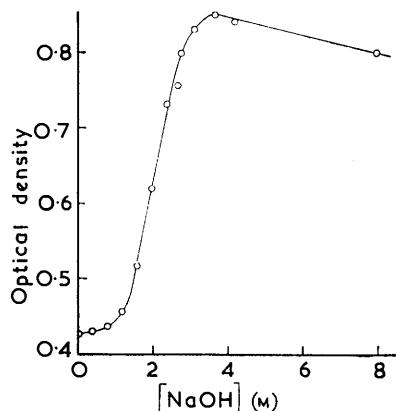


FIG. 2. Picric acid. Variation of initial optical density at 3900 Å with concentration of sodium hydroxide.

$[P]_{\text{stoich}} = 3.91 \times 10^{-5}\text{M}$ .

power of the hydroxide concentration, the general manner of variation being as in a titration curve (Fig. 2). The velocity of fading also depends on the concentration of hydroxide. The increase in rate is more rapid than the first power of the concentration but is not as sensitive

TABLE 1.

Summary of results for picric acid in absence of light;  $[\text{Picric acid}]_{\text{stoich}} = 3.91 \times 10^{-5}\text{M}$ .

[NaOH] (M)	$10^3 D_0$ (3900 Å)	$100\alpha_1$	$100\alpha_2$	$10^7 k^*$ (sec. <sup>-1</sup> )	[NaOH] (M)	$10^3 D_0$ (390 Å)	$100\alpha_1$	$100\alpha_2$	$10^7 k^*$ (sec. <sup>-1</sup> )
0	426	100	0	—	2.65	757	22.1	77.9	35.4
0.394	430	—	—	3.07	2.76	800	12.0	88.0	—
0.789	436	97.6	2.4	6.12	3.13	830	4.9	95.1	—
1.182	456	92.9	7.1	11.7	3.44	—	—	—	37.5
1.577	516	78.8	21.2	22.4	3.65	851	(0)	(100)	—
1.97	620	54.4	45.6	—	4.17	842	—	—	—
2.36	732	28.0	72.0	—	7.95	800	—	—	—
		NaOH (M)	$10^4 \epsilon$ (3400 Å)	$10^4 \epsilon$ (3800 Å)	$10^4 \epsilon$ (5500 Å)				
		1.43	1.200	1.319	0				
		2.64	0.839	1.833	0				
		3.22	0.764	1.972	0				

\* Graphically evaluated first-order rate constant of fading reaction at 40°.

TABLE 2.

Fading of picrate solution in sodium hydroxide at 40°; specimen run.

$[\text{Picrate}]_{\text{stoich}} = 3.91 \times 10^{-5}\text{M}$ ;  $[\text{NaOH}] = 1.182\text{M}$ .

Time (days) .....	0 *	1.92	4.04	6.79	10.77	15.74	40(∞)
$10^3 D_t$ (3600 Å) .....	559	490	413	341	250	195	100
$\log \{(D_0^* - D_\infty)/(D_t - D_\infty)\}/t$ (day <sup>-1</sup> ) .....	—	0.037	0.041	0.041	0.045	0.043	—

(Mean  $k_1 = 1.17 \times 10^{-6}$  sec.<sup>-1</sup>.)

\* First reading, after 0.04 day.

as the ratio  $\alpha_2/\alpha_1$ . A more gradual change (decrease) in optical density with hydroxide concentration supervenes beyond *ca.* 4M.

The spectrum of a solution of picric acid in 3.44M-sodium hydroxide after 15.8 days at 40° (reaction half-life = 2.1 days) showed maxima at 2700 and 3900 Å. Nitrite analyses on  $3.91 \times 10^{-5}$ M-solutions of picric acid (P) in sodium hydroxide after 8 weeks at 40° gave the following results:

[OH <sup>-</sup> ] (M) .....	1.58	2.65	3.44
100 [NO <sub>2</sub> <sup>-</sup> ]/[P] <sub>stoich</sub> .....	95	101	116

According to the rates of fading, the time interval chosen should represent 15, 24, and 26 half-lives, respectively, for the three concentrations. The figures show that close to one nitro-group is lost per molecule during the change of absorption spectrum, and that subsequent further loss of nitro-groups is slow by comparison.

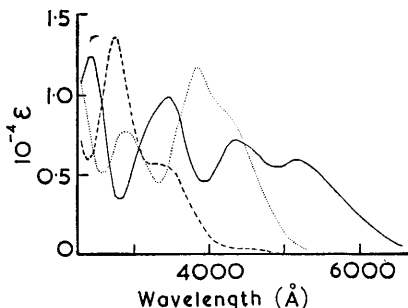


FIG. 3. 3,5-Dinitrocatechol. Absorption spectra.

Stoichiometric concentration:  $3.4 \times 10^{-5}$ M. Dotted line, water; broken line, 0.13M-hydrochloric acid; full line, 1.32M-sodium hydroxide.

Irradiation of picrate solutions with visible white light by the usual procedure caused a more rapid variation in optical density (first noted by Eisenbrand and von Halban<sup>3a</sup>) and formation of nitrite (Table 3). No nitrite was detectable in the "dark" solution after

TABLE 3.

Light-sensitivity of picrate solution ( $3.91 \times 10^{-5}$ M), in 2.61M-sodium hydroxide at 25°.

Time (min.) .....	3	60	420	1440
<i>D</i> (4100 Å) for reaction in dark .....	0.587	0.578	0.572	0.552
<i>D</i> (4100 Å) for reaction in light .....	0.588	0.542	0.434	0.333

TABLE 4.

Photochemical nitrite formation from picrate solution ( $3.91 \times 10^{-5}$ M) at different hydroxide concentrations at 25°.

[NaOH]	Time (hr.)	$10^5$ [NO <sub>2</sub> <sup>-</sup> ] * (M)
0.223	22	0.95
0.557	22	2.40
3.57	2	2.02

\* [NO<sub>2</sub><sup>-</sup>] is the difference between the concentration of nitrite found and that found in a corresponding sample protected from light.

1440 min., whereas a concentration of  $2.55 \times 10^{-5}$ M (0.65 NO<sub>2</sub> groups per molecule) was found in the irradiated solution. Photochemical nitrite formation occurs at various hydroxide concentrations (Table 4).

Fig. 3 records the observed spectra of 3,5-dinitrocatechol in aqueous hydrochloric acid, water, and aqueous sodium hydroxide solution. There are only very slight changes in the spectra on increasing the hydroxide concentration in the range 1.32—3.22M. The spectrum of the solution in 1.32M-sodium hydroxide was unchanged after 18.5 hr. in the dark, or after irradiation for 2.6 hr. The additional absorption bands in aqueous solution are attributed to the ion (I).

2,6-Dinitroquinol gives unstable solutions in alkali and initial optical densities were inferred by extrapolation to zero time. Spectra of the initial solutions and of the reaction products in

aqueous hydrochloric acid and aqueous sodium hydroxide are given in Figs. 4 and 5. The reaction which takes place in the dark was followed by observation of the disappearance of the band at 5500 Å and by the appearance of the band at 3400 Å. Identical first-order rate constants were obtained, indicating that there is no storage of an intermediate product. The variation of the rate constant at 25° and of extinction coefficients, at three wavelengths, of initial and product solutions as a function of hydroxide concentration are given in Table 5.

TABLE 5.

2,6-Dinitroquinol. Summary of rate constants for dark reactions and initial and final extinction coefficients at selected wavelengths.

[NaOH] (M)	10 <sup>5</sup> k at 25° (sec. <sup>-1</sup> )	10 <sup>-1</sup> ε <sub>0</sub> at			10 <sup>-1</sup> ε <sub>∞</sub> at		
		3400	3800	5500 Å	3400	3800	5500 Å
0.53	0.57	146	76	634	—	—	—
1.43	2.94	146	124	627	980	2080	7
2.64	29.4	529	236	607	887	2040	22
3.22	62.1	820	366	505	905	2000	12
3.62	106	—	481	—	—	1980	—

The rate of the "dark" reaction was increased by a factor of *ca.* 3 if oxygen was bubbled through the solution. This suggested that the observed reaction was the oxidation of 2,6-dinitroquinol to 2,6-dinitroquinone and that the spectra in Fig. 5 relate to the latter substance. (No reference to a dinitroquinone was found in the literature.) The reaction was not accelerated by light but the product spectrum changed slowly on irradiation (*ca.* 25% fading after 22 hr.).

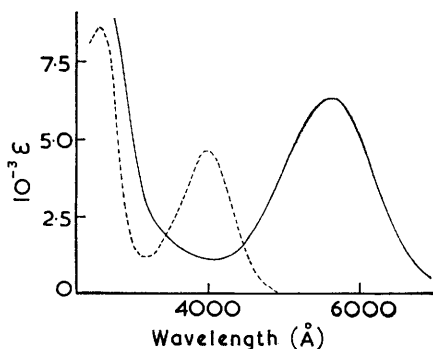


FIG. 4. 2,6-Dinitroquinol. Absorption spectra.

Broken line, 0.13M-hydrochloric acid;  
full line, 1.43M-sodium hydroxide.

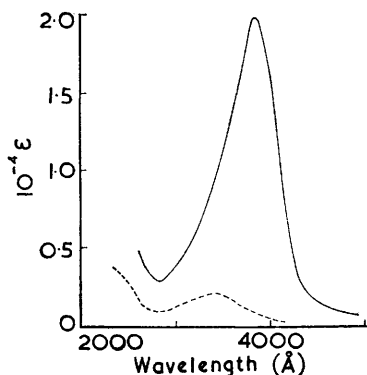


FIG. 5. Absorption spectra of product of dark reaction of 2,6-dinitroquinol (2,6-dinitroquinone?).

Broken line, 0.39M-hydrochloric acid;  
full line, 1.43M-sodium hydroxide.

## DISCUSSION

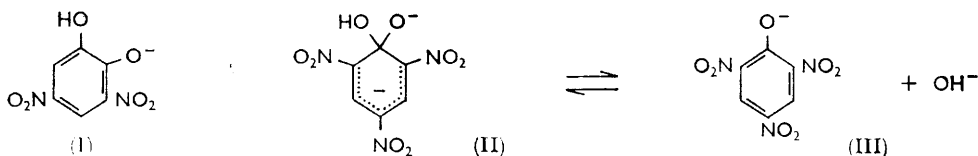
Picric acid undergoes at least two reversible reactions in aqueous alkali. The first of these gives rise to the picrate ion and is complete even in water for the low concentrations of picric acid used in this study. A significant fraction of picrate is converted into a "second complex" only at concentrations of sodium hydroxide approaching 1M and above (Table 1).

The second complex of picric acid differs from the corresponding complexes observed for the trinitrobenzene-hydroxide<sup>4c</sup> and dimethylpicramide-methoxide<sup>4c</sup> system where the absorption spectrum of the second complex is shifted to shorter wavelengths relative to that of the 1:1 complex. In the case of picric acid-hydroxide (and of methyl picrate-methoxide<sup>4a</sup>) the spectrum moves to longer wavelengths (Fig. 1). If the second complex

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has the structure (II), one would indeed expect it to resemble a 1 : 1 complex of trinitrobenzene rather than a 1 : 2 complex. (The model does not, however, explain the bathochromic shift in the system methyl picrate-methoxide.)

The steep dependence of the extent of conversion of picrate ion into the second complex on the concentration of sodium hydroxide (Table I) can hardly indicate the stoichiometry of that complex (in a conventional sense); approximately five hydroxide ions per picrate ion would have to be postulated. This behaviour is responsible for previously noted<sup>3a</sup> difficulties in the evaluation of a "second dissociation constant" of picric acid. Similarly, the velocity of the "dark" reaction (which appears to be the replacement of a nitro-group by a hydroxide group and formation of nitrite) shows a complex though somewhat less steep dependence on the hydroxide concentration, as does the conversion of the 1 : 1 complex between trinitrobenzene and hydroxide ion into a second complex.<sup>4e</sup> These observations relate to fairly concentrated solutions of alkali, where the neglect of activity coefficients, which is implicit in such a simplified analysis, must be suspect. One can formally side-step the problem of these activity coefficients by introducing the concept of acidity functions, which is successful for acid solutions provided that comparisons are confined to acid-base reactions of similar structural characteristics. On this basis, concentrated alkali solutions would be governed by acidity functions. The function appropriate to proton loss from an electrically neutral indicator acid<sup>8</sup> is  $H_-$ . Similarly, the  $J_-$  function<sup>9</sup> would regulate the equilibrium of hydroxide addition to an electrically



neutral substrate. An example of such behaviour would be the 1 : 1 complex formed from trinitrobenzene and sodium hydroxide (but in that case the colour change occurs in solutions sufficiently dilute for the concentration of hydroxide ion to be a satisfactory measure of the inverse acidity of the solution). An equilibrium [(II)  $\rightleftharpoons$  (III)] as is being contemplated in the present context,<sup>3b</sup> would be regulated by the  $J_-$  function. If this view of the nature of the second complex is correct, one should look upon the variation of  $\alpha_2/\alpha_1$  (Table I) as indicating the dependence of  $j_{2-}$  on the composition of the solution. A plot of  $\log(\alpha_2/\alpha_1)$  against Schwarzenbach and Sulzberger's  $H_-$  values<sup>8</sup> has a slope of 3.8. The fact that this slope is so unexpectedly steep leaves some doubt as to whether indeed only one further hydroxide particle is responsible for the formation of the second complex. Some more complex charge-transfer phenomenon<sup>10</sup> may be involved in this case.

The rate of the "dark" reaction does not exactly parallel either  $\alpha_2$  or  $\alpha_2/\alpha_1$  and can be approximately reproduced by the relation,

$$k = k_1\alpha_1[\text{OH}^-] + k_2\alpha_2,$$

with  $k_1 = 7.2 \times 10^{-7}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, and  $k_2 = 3.8 \times 10^{-6}$  sec.<sup>-1</sup>. In the light of the foregoing discussion, this empirical equation must not be interpreted too literally. However, it probably implies that more than one transition-state composition should be considered.

Two reaction paths are also indicated by the photochemical observations (Table 4). A photochemical reaction yielding nitrite is found both when  $\alpha_2 \sim 0$  and when  $\alpha_1 \sim 0$  (see Table 1), which means that both complexes can decompose on absorption of light. The

<sup>8</sup> Schwarzenbach and Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348.

<sup>9</sup> Gold and Hawes, *J.*, 1951, 2102; Gold, *J.*, 1955, 1263.

<sup>10</sup> Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801; *Rec. Trav. chim.*, 1956, **75**, 845; Briegleb and Czekalla, *Angew. Chem.*, 1960, **72**, 401; Foster and Mackie, *Tetrahedron*, 1961, **16**, 119.

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difference in rate indicated by the first two observations in Table 4 implies that, as in the other photochemical reactions reported, the excited picrate ion reacts with a further hydroxide ion to eject a nitrite ion.

Compared with trinitrobenzene, both the "dark" and "light" reactions of picrate solutions in aqueous sodium hydroxide are slow.

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[Received, November 13th, 1963.]

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