337. *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part VIII.*[1] *Behaviour of Picramide and* NN-*Dimethylpicramide in Aqueous Sodium Hydroxide.*

By V. Gold and C. H. Rochester.

At low concentrations of sodium hydroxide in water, picramide reacts with one hydroxide ion, and dimethylpicramide with two hydroxide ions, to form soluble complexes. The corresponding equilibrium constants have been measured. In both cases there is evidence of further interaction at higher hydroxide-ion concentrations. Attainment of the equilibrium is measurably slow for dimethylpicramide with very low hydroxide concentrations, and the kinetics of that reaction also require the complex to have 1 : 2 stoicheiometry. The establishment of the equilibrium is succeeded by a slower, irreversible hydrolysis in which picrate ions are formed. In the presence of visible light an additional reaction occurs as a result of which nitrite ions are liberated in solution and which ultimately leads to a mixture of 3,5-dinitrocatechol and a product of further reaction of 2,6-dinitroquinol (believed to be 2,6-dinitroquinone). The rates of these various reactions have been measured as a function of hydroxide ion concentration.

The anomalous nature of the 1 : 2 interaction of dimethylpicramide is pointed out.

Picramide ($PicNH_2$) and its *NN*-dimethyl derivative ($PicNMe_2$) give indicator colour changes in dilute aqueous solution. They also undergo further reversible and irreversible reactions, which differ in nature according to whether the solutions are exposed to light or not. The two compounds show significant differences between themselves, and their behaviour in aqueous sodium hydroxide is different from that in methanolic sodium methoxide solution.[1c] The pK value of picramide (ionization as an acid) in aqueous solution [2] (12·20) has served to define the course of the H_- function in basic media.[2,3] No corresponding study has been reported for the dimethyl derivative which, although it behaves as an indicator, possesses no acidic hydrogen atom, and cannot therefore be governed by H_- in its ionization.

Experimental

4-Amino-3,5-dinitrophenol (m. p. 236—237°; lit.,[4] 230—231°) was prepared by conversion of *p*-aminophenol into *ON*-diacetyl-4-aminophenol [5] (m. p. 150°; lit.,[5] 150—151°) followed by nitration to *ON*-diacetyl-4-amino-5,5-dinitrophenol (m. p. 228°; lit.,[4] 223—224°) and hydrolysis.

The preparation of other materials and solutions, and kinetic procedures, are, unless otherwise specified, the same as in previous work.[1] All kinetic results refer to 25°.

[1] 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; (*f*) Part VI, p. 1717; (*g*) Part VII, preceding paper.
[2] Stewart and O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493.
[3] Schaal, *J. Chim. phys.*, 1955, **52**, 784.
[4] Reverdin and Dresel, *Ber.*, 1905, **38**, 1593.
[5] Ladenburg, *Ber.*, 1876, **9**, 1528.

Absorption Spectra.—The spectra of picramide and of dimethylpicramide in different solutions (Figs. 1 and 2) correspond to indicator equilibrium without irreversible destruction of material having taken place. Acidification of a solution of picramide in 2·25M-sodium hydroxide and of a solution of dimethylpicramide in 1·18M-sodium hydroxide immediately after preparation resulted in complete reversion of the coloured species to the amine.

Attainment of Initial Equilibrium.—The formation of the initial coloured species from picramide was too rapid for observation but could be followed for dimethylpicramide by optical density measurements at 4100 Å (Fig. 3). Results at 25° (Table 1) satisfy the relation $10^3k = 0{\cdot}77 + 1{\cdot}45 \times 10^4[OH^-]^2$.

Equilibria.—For both substances, the equilibrium optical density (D_0) at 4100 Å was measured for different media (Tables 2 and 3), care being taken to ensure both complete attainment of equilibrium and negligible destruction by the irreversible secondary reaction, if necessary by making a short extrapolation from kinetic observations. In order to reduce the

TABLE 1.

Dimethylpicramide. Summary of rate constants for attainment of initial equilibrium at 25° (initial concentration = $2{\cdot}3 \times 10^{-5}$M).

10^3[NaOH] (M)	4·0	6·9	8·0	12·0	16·0
$10^3k'$ (obs.) (sec.$^{-1}$)	0·93	1·52	1·66	2·89	4·43
$10^3k'$ (calc.) * (sec.$^{-1}$)	1·00	1·46	1·70	2·86	4·48

* Calc. from the equation: $10^3k = 0{\cdot}77 + 1{\cdot}45 \times 10^4[OH^-]^2$.

possibility of a spurious effect due to carbon dioxide the measurements for dimethylpicramide were performed in alkaline media made up from different reagents (Table 4).

Formation of Picric Acid.—The slow reaction which follows the establishment of the initial equilibria leads for both compounds to solutions of picric acid (or picrate), provided light is

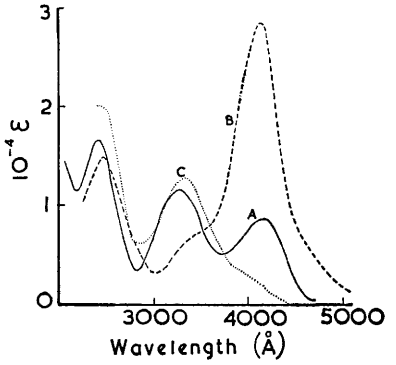


FIG. 1. Picramide. Absorption spectra in water and in sodium hydroxide solution ([$PicNH_2$] = $5{\cdot}24 \times 10^{-5}$M).

A, water; B, 0·59M-sodium hydroxide; C, 7·89M-sodium hydroxide.

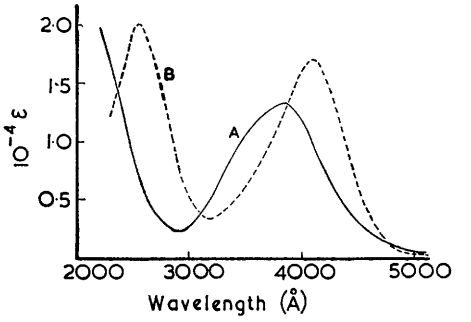


FIG. 2. *NN*-Dimethylpicramide. Absorption spectra in water and in sodium hydroxide solution ([$PicNMe_2$] = $2{\cdot}28 \times 10^{-5}$M).

A, water; B, 1·59M-sodium hydroxide.

excluded. The product was identified by the detailed agreement of spectra with those of solutions of picric acid at the same concentration of sodium hydroxide. These comparisons were made for picramide after reaction for 24 hr. in 0·59M- and for 23 hr. 7·95M-sodium hydroxide (the corresponding half-lives being 67 and 90 min., respectively), and indicated yields of 100 and 95%, respectively. The analogous observations for dimethylpicramide were for 4 hr. reaction (half-life 26 min.) in 1·59M-sodium hydroxide, the intensity of the spectrum corresponding to 98% yield. The absence of nitrite ion was confirmed by independent analyses. For both compounds the kinetics of this hydrolysis were followed by spectrophotometry at 4100 Å. Specimen runs are reproduced in Fig. 3. Rate constants are summarized in Tables 2 and 3. With both compounds, addition of sodium carbonate (0·15M) or passage

TABLE 2.

Picramide. Values of D_0 at 4100 Å and rate constants (k_2) for formation of picric acid at 25°.

[NaOH] (M)	D_0 * (exptl.)	D_0 † (calc.)	10^5k_2 (sec.$^{-1}$)	[NaOH] (M)	D_0 * (exptl.)	D_0 † (calc.)	10^5k_2 (sec.$^{-1}$)	[NaOH] (M)	D_0	10^5k_2 (sec.$^{-1}$)
0	0·442	—	—	0·01416	0·823	0·820	—	2·08	1·279	41·3
0·00024	0·445	0·451	—	0·0236	0·962	0·961	2·17	2·61	1·071	47·7
0·00059	0·463	0·464	—	0·0330	1·055	1·059	2·65	3·39	0·786	57·5
0·00083	0·465	0·474	—	0·0472	1·153	1·162	3·44	3·65	0·688	61·3
0·00119	0·482	0·486	—	0·0590	1·215	1·222	3·88	3·91	0·593	62·2
0·00142	0·497	0·496	—	0·118	1·367	1·379	5·86	4·77	0·373	62·0
0·00154	0·494	0·499	—	0·236	1·482	1·491	8·96	5·83	0·208	38·3
0·00166	0·500	0·504	—	0·476	1·544	—	13·9	6·89	0·168	25·2
0·00178	0·509	0·507	—	0·591	1·550	1·573	17·0	7·95	0·078	12·8
0·00472	0·599	0·601	—	1·182	1·504	—	28·3			
0·00944	0·726	0·722	—							

* For $[PicNH_2]_{stoich} = 5{\cdot}24 \times 10^{-5}$M. † Calc. from equation 3, with $m = 1$, $\varepsilon_A = 31{,}000$; $K_1 = 33{\cdot}1$ l. mole^{-1}.

TABLE 3.

Dimethylpicramide. Values of D_0 at 4100 Å and rate constants (k_2) for formation of picric acid at 25° in sodium hydroxide solutions.

10^3 [NaOH] (M)	D_0 *	D_0 (calc.) ‡	[NaOH] (M)	D_0 †	10^5k_2 † (sec.$^{-1}$)	[NaOH] (M)	D_0 †	10^5k_2 † (sec.$^{-1}$)
0	0·281	(0·281)	0·0118	—	1·80	1·93	0·386	54·0
4·0	0·362	0·362	0·026	0·408	2·37	2·36	0·378	66·5
8·0	0·461	0·471	0·064	0·426	3·44	2·79	0·375	66·0
10·0	0·510	0·526	0·127	0·421	5·90	3·14	0·378	67·5
12·0	0·530	0·535	0·215	0·439	9·7	3·92	0·373	69·0
16·0	0·561	0·570	0·645	0·414	24·4	4·71	0·357	72·9
50·0	0·624	0·621	1·075	0·396	35·2	5·94	0·375	78·6
			1·59	0·388	48·4			

* For $[PicNMe_2]_{stoich} = 2{\cdot}91 \times 10^{-5}$M. † For $[PicNMe_2]_{stoich} = 2{\cdot}13 \times 10^{-5}$M. ‡ Calc. from equation 3, using $m = 2$, $K_1 = 1{\cdot}89 \times 10^4$ l.^{2} mole^{-2}; ε_A (4100 Å) $= 2{\cdot}16 \times 10^4$.

TABLE 4.

Dimethylpicramide. Values of D_0 at 4100 Å in alkaline buffer solutions.

	(*a*) NaOH–KCl solutions				(*b*) NaOH–Na_2HPO_4 solutions				
$10^3[OH^-]$ *	*9·16*	*10·64*	13·12	19·45	3·44	5·64	8·26	11·25	*14·72*
D_0 †	0·499	0·518	0·552	0·588	0·355	0·425	0·490	0·525	0·561
D_0 (calc.) ‡	0·482	0·518	0·546	0·586	0·344	0·411	0·476	0·525	0·561

* Values calculated from data given by Bates and Bower, *Analyt. Chem.*, 1956, **28**, 1322; italicised values involve a short extrapolation. † $[PicNMe_2]_{stoich} = 2{\cdot}91 \times 10^{-5}$M. ‡ See corresponding footnote in Table 3.

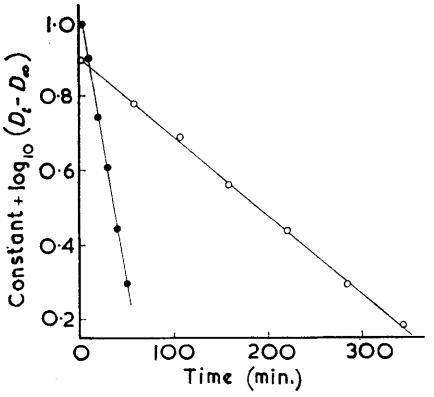


FIG. 3. Illustration of (" dark ") first-order formation of picric acid at 25°.

● Dimethylpicramide in 1·93M-sodium hydroxide.

○ Picramide in 0·236M-sodium hydroxide.

of oxygen through solutions had no effect on the reaction velocity or the values of D_0 and D_∞ at 4100 Å ([NaOH] = 1·64M for picramide, 1·00M for dimethylpicramide).

Photochemical Effects.—(*a*) *Experiments with white light* (tungsten filament lamp [1d]). The rate of variation of optical density at 4100 Å, for a solution containing $2{\cdot}62 \times 10^{-5}$M-picramide and 1·18M-sodium hydroxide, was speeded up *ca.* four times by the usual method of irradiation.[1d] After *ca.* ten half-lives (73 min.) the solution was analysed and found to contain $1{\cdot}77 \times 10^{-5}$M-nitrite, in approximate agreement with the hypothesis that the photochemical component of the total reaction produces one nitrite ion per molecule of picramide.

Analogous experiments with $1{\cdot}51 \times 10^{-5}$M-dimethylpicramide in 1·18M-sodium hydroxide (irradiation for 73 min., *i.e.*, *ca.* 4 half-lives) produced $0{\cdot}73 \times 10^{-5}$M-nitrite, again in agreement with the photochemical contribution to the total rate. To test whether this amount of nitrite might have been produced by photolysis of picrate ions (*i.e.*, the reaction product of the thermal

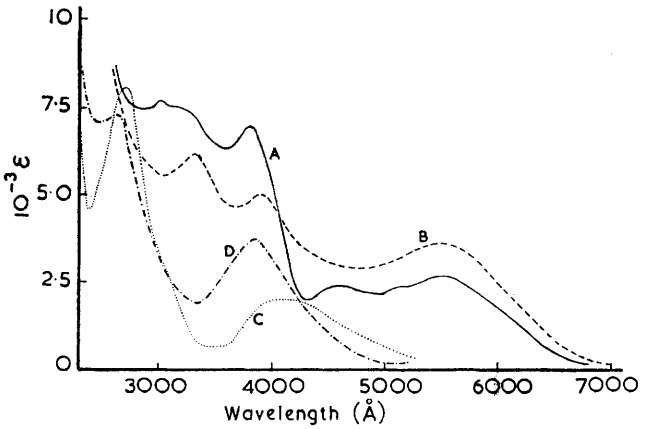


FIG. 4. Spectra of products of photochemical experiments (tungsten lamp) starting with picramide and dimethylpicramide.

A, Dimethylpicramide in 1·43M-sodium hydroxide; B, picramide in same; C, dimethylpicramide in 0·13M-hydrochloric acid; D, picramide in same.

reaction) a solution of picric acid ($1{\cdot}96 \times 10^{-5}$M) in 1·18M-sodium hydroxide was irradiated for 73 min., after which time it contained only $0{\cdot}50 \times 10^{-5}$M-nitrite. Thus, there is some contribution to the nitrite concentration from this subsequent reaction, but the main source of nitrite ion must have been the photochemical reaction of one of the species involved in the initial equilibria of picramide (and of dimethylpicramide) with aqueous sodium hydroxide. For both compounds the reactions remain first-order for irradiation in a 2-cm. cell at the concentrations studied.

Because of the consecutive "light" reaction of picric acid, it was impossible to obtain infinity readings of optical density or nitrite concentration. Estimates of these values, on the basis of the foregoing information and similar determinations, allowed a correlation of the extent of photochemical reaction of picramide as measured by the change in reaction velocity with that indicated by the concentration of nitrite. The results agreed within the experimental limits of accuracy, thus showing that there was no appreciable photochemical reaction not yielding nitrite.

The final spectra in photochemical runs (before much decomposition of picric acid had occurred), measured directly and after acidification, suggested that the main constituents of the final solutions were picric acid, 3,5-dinitrocatechol, and 2,6-dinitroquinol. In the case of picramide the following experiment showed the absence of hydrolysable organic amine at that stage. A continuous stream of nitrogen was passed through the solution being irradiated, a procedure previously shown to remove ammonia from an alkaline solution, and the solution was then analysed for hydrolysable amine by the phenol–hypochlorite reaction.[6] This analysis

[6] Russell, *J. Biol. Chem.*, 1944, **156**, 457; Snell and Snell, "Colorimetric Methods of Analysis," van Nostrand, New York, 1949, Vol. II, p. 818.

gave exact results with picramide. It involves treatment with hot alkali which would cause a displacement of ammonia from 2,4-dinitroaniline [7] and presumably also from 2,6-dinitroaniline, since 2,4- and 2,6-dinitro-substituents are similarly activating in reactions of this type.[8] The test was negative, and thus confirms the absence of amines with nitro-groups in these pairs of positions. The loss of the amino-group cannot precede the photochemical reaction of picramide; if it did, the photochemical effects would be confined to the action of light on picric acid. Since simultaneous photochemical hydrolytic loss of both a nitro-group and an amino-group is improbable, it follows that the latter reaction is subsequent to the photochemical reaction of picramide (cf. our observations on 4-amino-3,5-dinitrophenol given below).

The effects of carbonate and oxygen were investigated as for the " dark " reactions. Carbonate was again without effect but oxygen had a small effect on the final optical density of both substances which was consistent with the effect of oxygen on the reaction of 2,6-dinitroquinol in aqueous alkali.[1g]

(*b*) *Experiments with monochromatic light* (4358 Å). Light from a Mazda 125-watt Type MB lamp, run off a voltage stabilizer, was focused by lenses to give a sharp inverted image of the source inside the reaction vessel (a stoppered rectangular 1-cm. quartz spectrophotometer cell; capacity 3 ml.). A concave mirror was placed behind the lamp with the light source at its centre of curvature in order to increase the available intensity. A 5-cm. cell containing filter solution of sodium nitrite and cuprammonium sulphate [9] (isolating the 4358 Å line) was placed between the lenses and the reaction vessel. The cell was thermostatted by immersion in water at 25°, with one of its plane faces about 1 cm. from, and parallel to, a plane window in the thermostat wall, the rest of the optical system being outside the thermostat. The cell could always be returned to exactly the same position in the optical system.

In kinetic experiments, the cell containing a sample of solution was removed from the thermostat after irradiation for a certain time, dried externally, and placed in a spectrophotometer for determination of the optical density at relevant wavelengths. The solution was then discarded and a fresh sample irradiated for a different interval. For infinity readings, the optical densities of the same solution were re-determined several times, the cell being replaced for further irradiation after each reading, until constancy was obtained. The number of light quanta incident on the solution per second (Q_{4358}) was determined by actinometry [1] to be $4{\cdot}40 \times 10^{15}$.

Under these conditions the " dark " reaction constitutes a significant fraction of the total reaction. However, because the reactions remain first-order, the photochemical rate constant (k_3) can be evaluated by subtracting the " dark " rate constant (k_2) from the gross rate constant k_{obs} for irradiated solutions (Tables 5 and 6).

TABLE 5.

Picramide. Photochemical rate constants for irradiation by monochromatic light ($[PicNH_2]_{stoich} = 1{\cdot}75 \times 10^{-5}$M).

[NaOH] (M)	10^4k_{obs}* (sec.$^{-1}$)	10^4k_2 (dark) † (sec.$^{-1}$)	10^4k_3 (photochemical) (sec.$^{-1}$)	10^3k ‡	$10^3k/[OH^-]^2$
0·33	1·73	1·17	0·56	1·0	9
1·00	5·86	2·46	3·40	5·4	5·4
1·67	8·55	3·63	4·92	8·4	3·0
2·40	13·8	4·5	9·3	18·3	3·2
3·01	15·7	5·3	10·4	25·8	2·9
3·33	16·9	5·7	11·2	33·6	3·0

* Based on observations at 4100 Å. † Interpolated values from results in Table 2. ‡ Quantum efficiency [equation (1)].

The kinetic observations permit an unambiguous " infinity " reading after *ca.* ten half-lives, but continued observations over even longer intervals (and without continuing irradiation beyond the first stage) show that a further slow reaction also takes place. If, as has been concluded above, the reaction products include 2,6-dinitroquinol, this instability of the product

[7] Willgerodt, *Ber.*, 1876, **9**, 977.
[8] Parker and Read, *J.*, 1962, 3149.
[9] Bowen, *J.*, 1935, 76.

TABLE 6.

Dimethylpicramide. Photochemical rate constants for irradiation by monochromatic light ($[PicNMe_2]_{stoich} = 9{\cdot}9 \times 10^{-6}$M).

[NaOH] (M)	10^4k_{obs}* (sec.$^{-1}$)	10^4k_2 (dark) † (sec.$^{-1}$)	10^4k_3 (photochemical) (sec.$^{-1}$)
0·476	2·66	1·83	0·83
0·964	5·05	3·27	1·78
1·429	7·30	4·36	2·94
2·382	8·46	5·81	2·65
2·890	9·44	6·31	3·13
3·335	11·35	6·66	4·69

* Based on observations at 4100 Å and/or 4360 Å. † Interpolated values from results in Table 3.

spectra and their apparent sensitivity to the presence of oxygen are expected. The spectra of 2,6-dinitroquinol and its reaction product in alkali (presumably 2,6-dinitroquinone) and of 3,5-dinitrocatechol are known.[1g] It was therefore possible to test the hypothesis that the only organic products present in the solutions of photochemical experiments after complete reaction of picramide or dimethylpicramide are picric acid (from the " dark " reaction), 3,5-dinitrocatechol, 2,6-dinitroquinol, and the reaction product of 2,6-dinitroquinol. The proportion of picric acid was evaluated as the velocity of the " dark " reaction divided by the total reaction velocity in the presence of light. The proportions of the other three products were obtained from measurements of the optical densities at 3400, 3800, and 5500 Å for the products and the assumed components. The calculation then involved solution of three simultaneous equations (method A). For product solutions in which the slow consecutive reaction had gone to completion the calculation involved the solution of only two simultaneous equations (on the assumption that no 2,6-dinitroquinol remained in solution) (method B). Results are given in Tables 7 and 8. The fair agreement among the analyses based on methods A and B supports the identification of the slow consecutive reaction as the known slow reaction of 2,6-dinitroquinol and thus the chemical nature of the products.

TABLE 7.

Picramide. Product compositions for reaction in monochromatic light ($[PicNH_2]_{stoich} = 1{\cdot}75 \times 10^{-5}$M).

[NaOH] (M)	Analyt. method	PicOH *	DNC *†	DNQ *‡	$\frac{100DNQ}{DNQ + DNC}$	Sum of products *
1·43	A	40	6	41	88	87
1·43	B	40	7	42	86	89
2·64	A	33	7	49	88	89
2·64	B	32	9	50	85	91
3·22	A	34	6	55	90	95
3·22	B	33	5	57	92	95

* Amount of substance expressed as percentage of initial stoicheiometric concentration of substrate. † DNC = 3,5-dinitrocatechol. ‡ DNQ = Sum of amounts of 2,6-dinitroquinol and its oxidation product.

TABLE 8.

Dimethylpicramide. Product compositions for reaction in monochromatic light (all analysed by method B; footnotes as in Table 7).

[NaOH] (M)	PicOH *	DNC *†	DNQ *‡	100DNQ/(DNQ + DNC)	Sum of products *
1·43	68	6	24	80	98
2·64	68	10	24	71	102
3·22	67	8	26	76	101

Combination of the photochemical rate constants for picramide with the value of Q_{4358} and the extinction coefficient of the coloured complexes in solution leads to the quantum efficiency by application of the equation

$$\frac{d[NO_2]}{dt} = \frac{k}{NV} \cdot \frac{\varepsilon_\lambda^A \bar{C}^A}{D_\lambda} \cdot Q_\lambda (1 - 10^{-D_\lambda}) \qquad (1)$$

obtained by combining equations (3) and (5) of Part IV [1d] (Table 5). The symbols have the same meaning as before.[1d] The superscript A refers to the absorbing (first) complex of the amide, and the volume (V) is now 0·003 litres. The difference in kinetic form from the earlier photochemical results [1d] derives from the size of the factor $(1 - 10^{-D_\lambda})$. For the zero-order reactions this factor is close to unity, virtually all the incident radiation being absorbed by the excitable complex species, so that the rate of light-absorption becomes independent of the concentration of complex. In the present first-order runs, the absorption at the irradiating wavelength is comparatively small (partly because of the shorter length of cell), so that the factor $(1 - 10^{-D_\lambda})/D_\lambda$ remains practically constant during the course of a run, and the rate of light-absorption becomes proportional to the concentration of complex. Equation (1) can be applied to picramide on the assumption that absorption by picramide molecules is photochemically unimportant. It is known that the second complex, which predominates at high hydroxide concentrations, does not detectably absorb light at 4358 Å (Fig. 1). This is not true for *NN*-dimethylpicramide, and, in view of the results with picric acid,[1g] it is questionable whether only light-absorption by the first complex should be considered to be photochemically effective, and accordingly an analysis of the photochemical runs is not attempted.

Reaction of 4-Amino-3,5-dinitrophenol with Aqueous Sodium Hydroxide.—The rapid first-order destruction of the substrate was followed by spectrophotometric observations at 4900 Å (Table 9). A slower spectral change at 3800 Å occurs after completion of this reaction, and corresponds to the change which occurs in alkaline solutions of 2,6-dinitroquinol.[1g] The initial fast reaction was not affected by light from the tungsten lamp.

TABLE 9.

4-Amino-3,5-dinitrophenol. Rate constants for disappearance of absorption at 4900 Å in alkaline solutions at 25° (initial concentration = $1·21 \times 10^{-4}$M).

[NaOH] (M)	0·72	1·43	2·15	3·18
10^5k (obs.) (sec.$^{-1}$)	101	220	347	493
10^4k (obs.)/[OH$^-$]	14	15	16	15

DISCUSSION

The absorption spectrum of picramide in aqueous sodium hydroxide (Fig. 1) shows only minor differences from that in methanolic sodium methoxide.[1c] Dimethylpicramide is unusual in that its spectrum in aqueous sodium hydroxide resembles not the spectrum of the 1 : 1 complex formed with sodium methoxide but the " higher " complex, which probably has a 1 : 2 stoicheiometry. The observation suggests that the only complex formed from dimethylpicramide and hydroxide has a stoicheiometry other than 1 : 1. This inference is supported by the following more direct evidence.

The rate of formation of the complex prevalent at low hydroxide-ion concentration was measured in the case of dimethylpicramide by the build-up of the absorption spectrum on mixing the reagents. If the formation of the absorbing complex A is represented by the equilibrium

$$\mathrm{PicNMe_2} + m\mathrm{OH^-} \pm n\mathrm{H_2O} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{A}, \qquad (2)$$

(with $[\mathrm{OH^-}] \gg [\mathrm{PicNMe_2}]$ or [A]), the first-order rate constant k' for attainment of equilibrium is given by

$$k' = k_1[\mathrm{OH^-}]^m + k_{-1}.$$

The results (Table 1) require $m = 2$, and yield the equilibrium constant of reaction (2), $K_1 = k_1/k_{-1} = 1·45 \times 10^4/0·77 = 1·88 \times 10^4$ l.^{2} mole^{-2}.

The value of m was also obtained from the optical densities at a wavelength near the absorption maximum of A, measured after attainment of equilibrium but before irreversible secondary processes had become important. In each case the absorption rises steeply at low concentrations, passes through a maximum, and then declines. This behaviour is more marked for picramide (Table 2), presumably because the formation of a higher complex of dimethylpicramide is not attended by such a large change in extinction

coefficient (Table 3). The values after the maximum again relate to high hydroxide-ion concentrations and should be analysed in terms of acidity functions. The initial increase in D_0, on the other hand, concerns very dilute hydroxide solutions. These results can be treated in terms of the equation

$$(D_0 - \varepsilon_p[P]_{stoich})/[OH^-]^m = \varepsilon_A K_1[P]_{stoich} - K_1 D_0. \quad (3)$$

The significance of the symbols and derivation of this equation are analogous to those of equation (3a) of Part III.[1c] The experimental results are satisfied by $m = 1$ in the case of picramide (Table 2), with $K_1 = 32{\cdot}8$ l. mole^{-1} and ε_A (4100 Å) $= 3{\cdot}25 \times 10^4$; and $m = 2$ for dimethylpicramide; with $K_1 = 1{\cdot}89 \times 10^4$ l.^{2} mole^{-2} and ε_A (4100 Å) $= 2{\cdot}16 \times 10^4$. The agreement between this value of K_1 for dimethylpicramide and that derived from the rate of attainment of equilibrium supports the correctness of this analysis despite the unexpected stoicheiometry of the dimethylpicramide complex. In view of the diluteness of the sodium hydroxide solutions, and in order to eliminate the possibility that the unusual result was caused by inadequate elimination of carbon dioxide, three different kinds of alkaline media were used (Table 4), and substantially the same measurements obtained at comparable hydroxide concentrations. The results also eliminate the inclusion of the sodium cation in the coloured complex as an explanation of the square-dependence on sodium hydroxide concentration, since the experiments include cases for which $[Na^+] \neq [OH^-]$. Because of the different values of m in equation (2) picramide is more fully converted into complex than dimethylpicramide at hydroxide concentrations below $1{\cdot}75 \times 10^{-3}$M; at higher concentrations the reverse order holds.

The " dark " reactions of both picramide and dimethylpicramide lead quantitatively to picric acid. The " dark " reaction of picramide in methanolic sodium methoxide in which nitrite ions are liberated is thus unusual.[1c] The hydrolyses are slow reactions and were not followed at the low concentration of hydroxide for which only a single complex need be considered and in which activity coefficients may be ignored. Over a range of higher hydroxide-ion concentrations, the hydrolysis velocity of picramide increases beyond the concentration at which the maximum optical density is reached (Table 2), and at a very much higher hydroxide concentration the rate begins to fall. However, the rate variations are not large. Dimethylpicramide behaves similarly but a rate maximum was not observed. For these reasons only qualitative conclusions emerge from these rate measurements. They suggest that, for both compounds, the rate equation contains terms in both the first and the second complex, the latter species being less reactive.

The photochemical reactions with these two compounds give different products from the " dark " reactions. With both compounds a nitrite ion is formed, and the absorption spectra indicate that the final products of the reaction are 3,5-dinitrocatechol and 2,6-dinitrobenzoquinone. The overall change entails hydrolytic loss of the amino- or dimethylamino-group subsequently to the photochemical hydrolysis of the nitro-group, the 2,6-dinitroquinol being oxidized by dissolved oxygen. The kinetics require that the postulated secondary hydrolysis must be a rapid reaction. This is supported by the observation that the hydrolysis of 4-amino-3,5-dinitrophenol (one of the implied intermediates formed by the photochemical loss of the nitro-group from picramide) is much faster than the formation of 2,6-dinitroquinol from dimethylpicramide. Since the leaving tendencies of amino- and dimethylamino-groups in nucleophilic substitution (Tables 2 and 3) are similar, it is fair to conclude that the hydrolysis of 4-*NN*-dimethylamino-3,5-dinitrophenol would likewise be a rapid reaction, as required by this scheme.

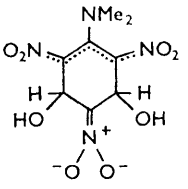
The final products are formed in different proportions for the two compounds, the nitro-group in the *para*-position being more reactive in both cases (Tables 7 and 8).

The quantum yield k for picramide, evaluated from equation (1), increases roughly as the square of the hydroxide concentration (Table 5). In view of the high concentrations

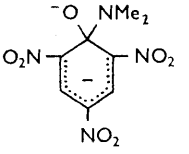
involved, activity coefficient considerations complicate the picture. The result probably implies that the rate-limiting step is analogous to that for similar reactions in methanol solution,[1d] and involves an excited molecule of the complex and one further hydroxide ion.

Although the foregoing discussion systematizes the experimental results it does not solve the central problem, of the nature and structure of the complexes. In preceding Parts the situation was generally clear for low concentrations of base; a 1 : 1 complex was formed and, by stepwise relation to the methyl picrate–methoxide complex, probable structures were proposed. Sometimes there is evidence for complexes of higher stoicheiometry but the same kind of structure may not hold in every case.

The dimethylpicramide–hydroxide system is the only one for which 1 : 1 interaction with lyate could not be detected. (The case for 1 : 1 interaction between dimethylpicramide and methoxide is based on comparatively few results [1c] and does not appear as strong as that for reversible 1 : 2 interaction with hydroxide.) Structures in which two hydroxide ions are added [such as (I)] or in which there is hydroxide addition and



(I)



(II)

proton loss [such as (II)] are formal possibilities for the 1 : 2 complex, but they do not satisfactorily account for one or more of the following observations: (1) the non-appearance of a 1 : 1 complex; (2) the appearance of a 1 : 1 complex between sodium hydroxide and trinitrobenzene or picramide; (3) the similarity of the absorption spectrum of the 1 : 2 complex and the higher complex (1 : 2 ?) between dimethylpicramide and sodium methoxide. Some unorthodox type of interaction is suspected but the evidence is insufficient to establish its nature. Whatever the interaction is, it still produces photochemical lability of the nitro-groups.

We thank the D.S.I.R. for a studentship (C. H. R.) and for a research grant in support of the work of this series. Our thanks are also due to Professor W. G. Style for his interest and advice on chemical matters.

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