335. *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part VI.[1] The Photochemical Hydrolysis of 1,3,5-Trinitrobenzene.*

By V. Gold and C. H. Rochester.

The rate of disappearance of 1,3,5-trinitrobenzene from solutions in aqueous alkali is accelerated by light. The products of the photochemical reaction are nitrite and 3,5-dinitrophenoxide ions ($>90\%$), the balance of organic material probably being picrate. The apparent quantum yield of the reaction increases with the concentration of sodium hydroxide, indicating that electronic excitation of the absorbing 1 : 1 complex between trinitrobenzene and hydroxide ion is followed by further reaction of the excited species with hydroxide ions.

The dependence of the rate of the photochemical reaction on the wavelength of monochromatic light shows that excitation occurs by absorption of radiation in the longest wavelength absorption region of the 1 : 1 complex, but it also appears that not the entire absorption region is associated with the photochemically effective electronic transition.

Specific mechanistic models of the reaction are briefly considered.

IT was noted by Eisenbrand and von Halban[2] and confirmed by Čůta and Písecký[3] that solutions of 1,3,5-trinitrobenzene in alkali fade more rapidly when they are exposed to light. We have already briefly reported[4] that the reaction accelerated by light is the loss of a nitro-group (as nitrite ion) and conversion of trinitrobenzene into the 3,5-dinitrophenoxide ion. The present Paper deals more fully with the investigation of the mechanism of this reaction. The simple stoicheiometry of this photochemical reaction makes it more suitable for this purpose than the photochemical reactions of nitro-compounds in methanol solution.[5]

EXPERIMENTAL

The preparation of solutions, and analytical procedures, have already been described.[1]

The method of irradiation of samples with white light was the same as in previously reported work on methanol solutions.[5] In one experiment the normally used 2-cm. cell was replaced by a 10-cm. cell of equal area of cross-section.

The progress of the reaction under irradiation with white light, indicated by the change in optical density at 4400 Å, agrees fairly well with the rate of nitrite liberation (Table 1). This is in contrast to the gross disparity in the case of the " dark " reaction (Part V,[1] Table 3). There is a large increase in rate on irradiation. In one run the formation of nitrite ion was followed for a reaction in which illumination occurred only during a portion of the time. When the lamp was switched off the reaction reverted to its initial " dark " rate.

The absorption spectrum of the product solution (full curve in Fig. 1) corresponds to the formation of 3,5-dinitrophenoxide and nitrite ions in equivalent concentration. In this experiment the initial concentration of trinitrobenzene was 3.55×10^{-5}M and the final concentration of nitrite was 3.25×10^{-5}M (91.5% of the amount corresponding to complete replacement of one nitro-group). The broken curve is the absorption spectrum of a 3.25×10^{-5}M solution of 3,5-dinitrophenoxide ion. The circles in Fig. 1 are calculated from the same spectrum with the added assumption that the balance of organic product (8.5%) is picrate ion (3×10^{-6}M). The spectra of the two products were measured at the same hydroxide concentration as that of the reaction medium.

[1] Part V, preceding paper.
[2] Eisenbrand and von Halban, *Z. phys. Chem.*, 1930, **146**, 111.
[3] Čůta and Písecký, *Chem. listy*, 1957, **51**, 433; *Coll. Czech. Chem. Comm.*, 1958, **23**, 628.
[4] Gold and Rochester, *Proc. Chem. Soc.*, 1960, 403.
[5] Gold and Rochester, Part IV, *J.*, 1964, 1704.

The reaction curves were analysed in terms of the equation

$$d[NO_2^-]/dt = kS/NV. \qquad (1)$$

The integration for the evaluation of S covered the wavelength range 3500—6000 Å [for derivation and symbols of eqn. (1), see ref. 5]. The apparent quantum yield, k, calculated

TABLE 1.

Rates of fading and nitrite formation (irradiation by white visible light).

$[TNB]_{stoich} = 7.5 \times 10^{-5} M.$

Time (min.)	D_t (4400 Å)	% reaction Fading *	Nitrite † formation	$10^{-14} R$ ‡	$10^{-16} S$	$100k$
		(a) [NaOH] = 0.73M				
0	1.194	—	—	3.15	2.82	1.11
5	1.000	18.4	19.1	3.09	2.72	1.13
10	0.795	37.4	35.8	2.93	2.47	1.18
20	0.437	71.3	70.3	1.55	1.44	1.07
30	0.224	91.6	91.1	0.99	0.73	1.35
40	0.153	98.1	97.1	0.155	0.19	0.82
110(∞)	0.135	(100)	(100)	—	— (Mean) §	1.12
		(b) [NaOH] = 1.46M				
0	0.908	—	—	5.80	2.66	2.18
2	0.786	15.6	16.1	5.75	2.49	2.31
5	0.631	31.9	33.3	5.34	2.23	2.39
10	0.460	59.8	67.4	4.07	1.78	2.29
15	0.262	84.8	90.9	1.92	0.95	2.02
20	0.188	93.2	93.4	0.86	0.46	1.87
60(∞)	0.136	(100)	(100)	—	— (Mean §	2.24
		(c) [NaOH] = 2.72M				
0	0.495	—	—	7.70	2.07	3.72
2	0.417	20.4	17.7	7.65	1.84	4.15
5	0.339	43.4	45.0	6.06	1.54	3.94
10	0.229	72.4	77.4	3.28	0.89	3.68
15	0.174	89.4	92.0	1.64	0.40	4.10
20	0.153	95.5	99.7	0.86	0.19	4.5
60(∞)	0.131	(100)	(100)	—	— (Mean §	3.90

* Percentage of reaction = $100(D_t - D_0)/(D_\infty - D_0)$.   † Percentage of reaction = $100[NO_2^-]/[NO_2^-]\infty$.   ‡ $R = NV d[NO_2^-]/dt$ (molecules sec.$^{-1}$).   § Values above 90% reaction are excluded.

TABLE 2.

Dependence of apparent quantum efficiency (k) on concentration of sodium hydroxide.

[NaOH] (M)	0.73	1.46	2.72
k (mean)	0.011₂	0.022₄	0.039
$k/[NaOH]$	0.015	0.015	0.014

TABLE 3.

Reaction velocities for irradiated cells of higher optical density.

(a) [NaOH] = 0.71M; $[TNB]_{stoich} = 3.75 \times 10^{-4} M$; 2-cm. cell

Time (min.)	15	20	40	60	80	100	185
Percentage of reaction (exptl.) *	13.3	19.9	35.1	55.7	63.9	79.5	(100)
(calc.)	15	20	40	59	76	90	

(b) [NaOH] = 0.71M; $[TNB]_{stoich} = 7.5 \times 10^{-5} M$; 10-cm. cell

Time (min.)	30	60	90	115
Percentage of reaction (exptl.) †	27.0	50.0	70.1	77.5
(calc.)	30	59	85	95

* $100[NO_2^-]/[NO_2^-]\infty$.   † $100(D_t - D_0)/(D_\infty - D_0)$.

View Online

[1964] *Nitro-compounds in Alkaline Media. Part VI.* 1719

from the experimental data in Table 1 is proportional to the concentration of sodium hydroxide (Table 2).

In two experiments the conditions were changed so as to increase the optical density by a factor of five. In the first of these the path-length of the reaction cell was increased to 10 cm.; in the second, the initial concentration of trinitrobenzene was increased by a factor of five, the usual 2-cm. cell being used (Table 3). On the basis of eqn. (1), and using the proportionality between k and the hydroxide ion concentration (Table 2) to calculate the appropriate value of k, it is possible to predict the expected reaction curves of Table 3. These predictions are given in the last line of each portion of Table 3. The agreement between prediction and calculation is good near the beginning of each of these runs but gets progressively worse as the reaction progresses. This departure is in qualitative agreement with the expectation that, in these systems of higher optical density, absorption by product would constitute a progressively greater fraction of the total light-absorption in the cell, whereas for the runs
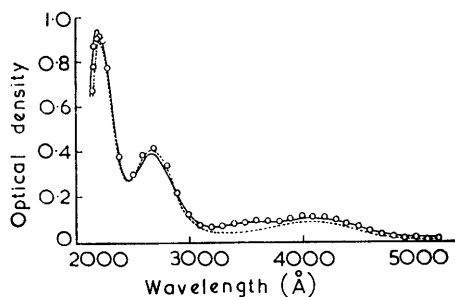

FIG. 1. Product spectrum.

Full curve: spectrum of 3.55×10^{-5}M-solution of trinitrobenzene after complete reaction in aqueous sodium hydroxide.
Broken curve: spectrum of 3.25×10^{-5}M-3,5-dinitrophenol in aqueous sodium hydroxide.
Circles: spectrum of solution containing 3.25×10^{-5}M-3,5-dinitrophenol and 3×10^{-6}M-picric acid in aqueous sodium hydroxide.
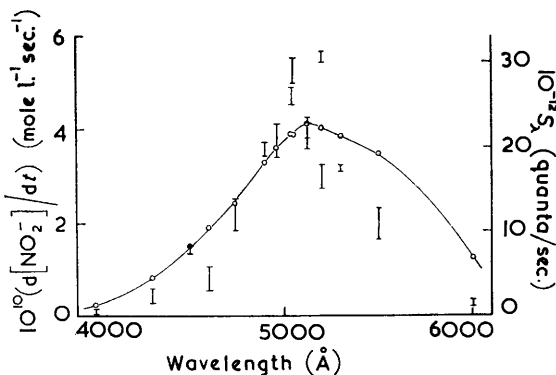

FIG. 2. Dependence of reaction velocity on wavelength.

Vertical lines: rate measurements (with limits of error), left-hand ordinate.
Full curve: values of S_λ, right-hand ordinate.

detailed in Table 1 this absorption by product remains fairly insignificant throughout a run. The good agreement for the initial rates in the runs of Table 3 confirms the applicability of eqn. (1).

The approximate dependence of the reaction velocity on wavelength was examined by placing the solution in the sample beam of a Unicam S.P. 600 spectrophotometer with a thermostatic cell compartment (25°) and following the optical density at 4400 Å as a function of time of irradiation for different wavelength settings of the instrument. The solution was stirred at regular intervals and immediately before each reading. The number of quanta of light incident on the solution per sec. (Q_λ) for different settings of the wavelength drum in the range 4000—4400 Å was determined by actinometry using a potassium ferrioxalate solution.[6] The energy emitted by the source both inside and outside this range was measured with a thermopile (Hilger and Watts FT 20.301) used in conjunction with an amplifier (Barr and Stroud). These relative measurements were converted into values of Q_λ on the basis of the results in the region for which both actinometric and thermopile measurements were made. Because of the low intensity of irradiation under the conditions of these experiments the rate measurements are not as precise as those for irradiation with white light. The initial rates

[6] Parker, *Proc. Roy. Soc.*, 1953, *A*, **220**, 104; Hatchard and Parker, *ibid.*, 1956, *A*, **235**, 518.

(corrected for the simultaneous " dark " reaction), expressed as $d[NO_2^-]/dt$ (vertical lines) and values of Q_λ (continuous curve), are plotted against wavelength (Fig. 2).

DISCUSSION

The experiments with a tungsten filament lamp indicate that the quantum efficiency of the reaction increases in proportion to the concentration of sodium hydroxide (Table 2). This result is formally analogous to that obtained with, for example, methyl picrate in methanolic sodium methoxide under the same conditions of irradiation. A similar reaction scheme, A having structure (I), can be written:

$$A \underset{-2}{\overset{2(+\,h\nu)}{\rightleftharpoons}} A^* \tag{2}$$

$$A^* + OH^- \xrightarrow{3} NO_2^- + (NO_2)_2C_6H_3 \cdot O^- \tag{3}$$
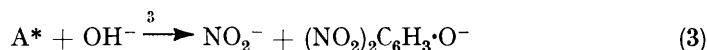
[cf. equations (7) and (8) of ref. 5]. The quantum efficiency is given by

$$k = k_3[OH^-]/(k_{-2} + k_3[OH^-]), \tag{4}$$

if the alkali concentrations are low enough for the distinction between acidity functions and concentrations to be neglected. On this basis the linear dependence of k upon $[OH^-]$ (Table 2) would indicate $k_{-2} \gg k_3[OH^-]$ over the concentration range studied, with $k_3/k_{-2} = 0.015$ l. mole^{-1}.

However, this interpretation is probably too simple, since h_-^{-1} increases more rapidly than the first power of the concentration of sodium hydroxide [7] above *ca.* 1·5M. K_w/h_- should therefore replace $[OH^-]$ in equation (4), if h_- is the appropriate acidity function. The fact that k increases less rapidly than in proportion to h_-^{-1} at the higher hydroxide concentrations then requires k_{-2} to be comparable to $k_3 K_w/h_-$ which, in turn, implies that the quantum efficiency cannot be far below its maximum value of unity. The fact that the values of the apparent quantum efficiency (Table 2) are appreciably below unity does not necessarily invalidate this line of reasoning, on the following grounds.

The variation of the reaction velocity with wavelength establishes that the photochemical effect is associated with absorption of light in the region of the longest-wavelength absorption of the 1 : 1 complex A. However, the photochemical effect does not appear to extend over the entire region of absorption in the visible region (Fig. 2). Other evidence suggests [5] that the broad absorption about 4500 Å is due to more than one electronic transition. The results of Fig. 2 make it probable that only one of these transitions is photochemically effective.

It follows that the evaluation of quantum yields (and hence of k_3/k_{-2}) on the assumption that all light absorbed between 3500 and 6000 Å produces the reactive excited state is incorrect. Only the fraction of radiation able to cause the relevant excitation ought to be included. The true quantum efficiency of the transition of interest may therefore have a value closer to unity than the tabulated apparent values (Table 2).

Step (3), which must involve a further molecule of base after the excitation of the 1 : 1 complex, may be the bimolecular substitution of nitrite by hydroxide, by analogy with the corresponding reactions with methanolic sodium methoxide.[5] A further possibility arises from the potentially acidic character of the hydroxyl group present in the 1 : 1 complex (and therefore does not exist for the reactions in methanol solution), as in the scheme (II) $\rightleftharpoons$ (III) $\longrightarrow$ (IV).

[7] Schwarzenbach and Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348.

View Online

[1964] *Nitro-compounds in Alkaline Media. Part VI.* 1721

Such a process might well be accelerated by light, for, by analogy with other hydroxylic organic compounds,[8] electronic excitation of (II) might strengthen its acidity to make the quasi-equilibrium concentration of the electronically excited ion (III*) much higher than that of (III). The scheme requires a sufficient fraction of the 1 : 1 complex to have
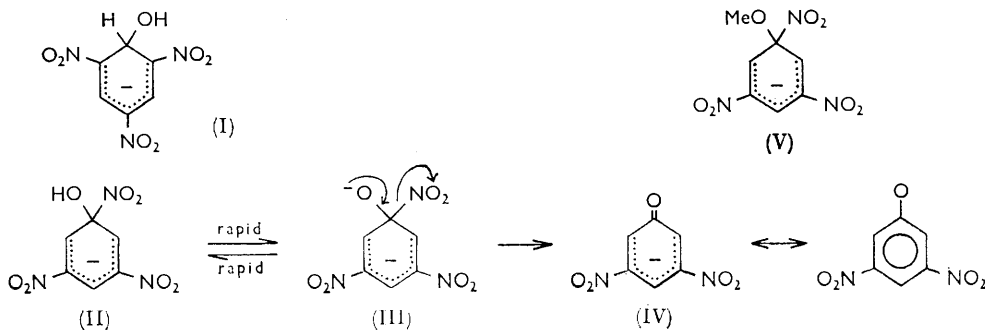
structure (II) so as to absorb light at a rate compatible with the observed reaction velocity. This would be satisfied if most of the 1 : 1 complex had structure (I) but that a small proportion of (II), having an absorption band in the region indicated by the experimental points in Fig. 2, is converted into product with a high quantum efficiency.

This scheme does not require us to attribute a large equilibrium concentration to structure (II), as proposed by Abe[9] to explain the formation of 3,5-dinitrophenol in the " dark " reaction. This is improbable since the very low speed of the " dark " hydrolysis would require the postulate that loss of hydroxide from (II) is a much more likely event than loss of nitrite. The implied relative anionic leaving tendencies of these groups are unlikely in view of the conclusion that the complex (V) (the analogue of II) must be in low concentration despite the fact that the replacement of a nitro-group in trinitrobenzene by methoxide is a fairly rapid reaction. The elimination of methoxide is therefore not favoured relative to nitrite. Since the hydroxide group is eliminated from similar structures less rapidly than an alkoxide group[1] it is not expected to leave (II) more readily than the nitrite group.

Structure (I) is also likely to experience an increase in acid strength as a result of electronic excitation but it would require unusual mechanistic ideas to make this effect responsible for the photochemical reaction observed.

KING'S COLLEGE, STRAND, LONDON W.C.2.

[8] Weller, *Z. Elektrochem.*, 1952, **56**, 662; 1954, **58**, 849.
[9] Abe, *Bull. Chem. Soc. Japan*, 1959, **32**, 339.