

333. *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part IV.*¹ *Photochemical Reactions in Methanolic Sodium Methoxide Solutions.*

By V. GOLD and C. H. ROCHESTER.

The loss of a nitro-group from methyl picrate, picric acid, and picramide is caused or accelerated by irradiation, with visible light, of methanolic solutions of 1:1 complexes between nitro-compound and methoxide. No corresponding effect could be detected for 1,3,5-trinitrobenzene or *NN*-dimethylpicramide. The quantum efficiencies of the reactions increase with concentration of methoxide, indicating that the transition state of the photochemical reaction involves two methoxide particles per molecule of nitro-compound. It is concluded that the absorption of light produces an excited state in which the negative charge in the complex is displaced towards the periphery of the molecule, thus leaving carbon atoms adjacent to nitro-groups more positive and susceptible to attack by a nucleophilic reagent than in the unexcited state.

At an early stage in the course of these investigations it was found that exposure to light lowers the stability of alkaline solutions of aromatic nitro-compounds.² For this reason a distinction was kept throughout between results obtained under strict exclusion of light ("dark" reactions) and those from solutions which were exposed to light under controlled conditions. Parts I³—III¹ related to the former conditions, and the present Paper deals with the effect of light on solutions of *sym*-trinitro-compounds. In addition to the derivatives discussed in Parts I—III, the present study includes picric acid, which is present in our solutions as the picrate ion and undergoes no further reversible or irreversible reaction with methoxide ion (at least up to 0.5M-sodium methoxide) in the dark. On exposure to light, these picrate solutions show certain features of the behaviour of the other compounds.

The instability of these or similar solutions to light has been briefly mentioned by a number of investigators but the present studies are believed to be the first concerned with the reaction which takes place.

EXPERIMENTAL

Picric acid (AnalaR) was recrystallised from ether. The preparation of other reagents and solutions has been described. Solutions were usually tested for light-sensitivity by measuring optical density of, or concentration of nitrite in, samples removed from two thermostatted flasks which contained initially the same solution; one of these was shielded from light whereas the other was placed two inches from a 150 w tungsten filament lamp run under normal conditions. Solutions which behaved in identical fashion under these conditions are in the following considered not to be light-sensitive, a description which refers only to the limits of detection of this procedure. Solution of 1,3,5-trinitrobenzene and dimethylpicramide in presence of methoxide ions are not light-sensitive by this criterion (see below). These two compounds decompose more rapidly in the dark than those compounds (picric acid, methyl picrate, and picramide) for which a light-sensitivity was readily detectable. The results do not exclude the possibility that comparable light-sensitivity is shared by all compounds but that it is not detectable for the two compounds having rapid "dark" reactions.

The light-sensitive solutions were further studied with a more exactly defined experimental arrangement: a cylindrical quartz cell of 2-cm. path-length and 12 ml. capacity was filled with solution and irradiated through one of its end faces by light from a 150 w tungsten-filament lamp run at the nominal voltage. The inlets of the cell were closed, and the cell and the lamp were immersed in a water thermostat. Undesired stray light was excluded from the side of the vessel by opaque material and from the end faces by cylindrical guard tubes, one of which extended close to the lamp. After a measured time, the cell was removed from its support and the entire

¹ Part III, preceding paper.

² Gold and Rochester, *Proc. Chem. Soc.*, 1960, 403.

³ Gold and Rochester, *J.*, 1964, (a) Part I, 1687; (b) Part II, 1692.

contents were emptied, stirred, and then either examined spectrophotometrically or analysed for nitrite.³ A fresh sample of solution was then placed in the cell for irradiation for a different period, and the whole procedure repeated for a series of time intervals. The location of the cell relative to the light-source and guard tube was exactly reproducible, and the cell always contained the same volume of solution. The mean intensity of light incident on the solution was therefore constant for all readings and for all reactions studied by this technique.

The number of quanta of light of a given wavelength, λ , incident on the cell was calculated approximately on the basis of figures for the energy distribution of the light for 100 and 200 tungsten filament lamps.⁴ If $n_\lambda d\lambda$ is the fraction of the total power (P erg sec.⁻¹) converted by the lamp into light within the range $d\lambda$ at a wavelength λ , and if ϕ represents the fraction of radiation from the lamp travelling in a solid angle so as to reach the cell, then $\phi n_\lambda P d\lambda$ will be the energy in the range $d\lambda$ reaching the cell per second. The corresponding number of quanta is $Q_\lambda = \phi n_\lambda P \lambda d\lambda / hc$ (where h is Planck's constant and c is the velocity of light. The parameter ϕ (which is constant for all wavelengths) was calculated, from the geometry of the experimental arrangement, as 0.0078; it is not known with high precision since a filament is not a point source at the centre of the bulb, as assumed in this calculation.

The number of light-quanta of a certain wavelength absorbed by the solution per second (S_λ) is then given by

$$S_\lambda = Q_\lambda(1 - 10^{-D_\lambda}). \quad (1)$$

If A is the only species absorbing light at wavelength λ , the optical density, D_λ , is given by

$$D_\lambda = \epsilon_\lambda^A \int_0^l C_x^A dx,$$

where C_x^A is the concentration of A in the cell at a distance x from the face nearer the light source, l is the length of the cell, and ϵ_λ^A the extinction coefficient of A at λ . The optical density can also be expressed in terms of the mean concentration \bar{C}^A of A,

$$D_\lambda = \epsilon_\lambda^A \bar{C}^A l, \quad (2)$$

irrespective of whether there is a concentration gradient of A in the direction x or not. If there is also slight light-absorption by product or any other species which does not result in excitation of A (an "inner filter"), equation (1) can be modified to give,

$$S_\lambda = [(\epsilon_\lambda^A \bar{C}^A) / D_\lambda] Q_\lambda (1 - 10^{-D_\lambda}). \quad (3)$$

This equation strictly applies only to stirred systems (in which C^A does not change along x), and can be justified for the unstirred, freely diffusing systems used by us only because the factor $\epsilon_\lambda^A \bar{C}^A D_\lambda$ was never far from unity.

For irradiation by white light, equation (3) was integrated over the long-wave absorption band of A considered responsible for the excitation (between λ_1 and λ_2 , say). Because of the glass envelope of the light-source it is certain that absorption bands at shorter wavelengths do not have to be considered. Hence, we obtain for the number of light-quanta in the effective frequency region absorbed per second

$$S = \bar{C}^A \int_{\lambda_1}^{\lambda_2} [(\epsilon_\lambda^A Q_\lambda) / D_\lambda] (1 - 10^{-D_\lambda}) d\lambda. \quad (4)$$

The integral was evaluated graphically for each compound. The least reliable part of this calculation is the factor Q_λ which depends on the geometry of the system and the characteristics of the light-source, and is probably not known more reliably than within a factor of two. However, since the experimental arrangement was accurately reproducible from one experiment to the next, and, since the absorption bands of the complexes were in the same spectral region, comparable uncertainties do not attach to comparative results between different compounds or,

⁴ Landolt-Börnstein, "Zahlenwerte und Funktionen," Springer-Verlag, Berlin, 1957.

even more so, between different runs on the same compound. The reaction velocities are expressed in terms of the quantum efficiency, k , defined by the equation

$$d[\text{NO}_2^-]/dt = kS/NV, \quad (5)$$

where N is Avogadro's number and V (0.012 l.) is the volume of the cell.

Results for individual compounds are detailed below. It should be noted that the quoted optical densities refer to 1-cm. path-length, although a 2-cm. cell was used for irradiations.

1,3,5-Trinitrobenzene.—Irradiation of a 0.40M-methoxide solution of trinitrobenzene ($5.9 \times 10^{-5}\text{M}$) produced no detectable difference in the spectrophotometric rate constant.

NN-Dimethylpicramide.—Light-sensitivity tests gave negative results for spectrophotometric rate constants (Table 1). Fig. 6 of Part III¹ explains the choice of the two methoxide concentrations used.

TABLE 1.

Light-sensitivity test for NN-dimethylpicramide.

[OMe ⁻]	10% k (sec. ⁻¹) (dark)	10% k (light)	D_0 (dark)	D_0 (light)
0.186	76	75	0.159	0.159
0.93	6.9	6.9	0.031	0.031

TABLE 2.

Light-sensitivity test for methyl picrate.

[OMe ⁻]	4100 Å			4800 Å		
	D_0	D (dark) after 6 hr.	D (light)	D_0	D (dark) after 6 hr.	D (light)
0.140	0.782	0.781	0.771	0.511	0.512	0.511
0.466	0.788	0.770	0.664	0.521	0.509	0.449
0.699	0.790	0.789	0.552	0.523	0.521	0.373
0.932	0.800	0.797	0.439	0.533	0.532	0.298

TABLE 3.

Correlation of fading with nitrite formation for "light" reaction of methyl picrate.

[OMe ⁻] (M)	Time of irradiation (hr.)	100($D_0 - D$)/ D_0		100[NO ₂ ⁻]/[P] ₀ (initial)
		at 4100 Å	at 4800 Å	
0.186	114	32	31	39
0.935	6	45	44	48
0.935	24	90	89	87

Methyl Picrate.—The complete absorption spectrum of the solution corresponding to the liberation of 0.90 nitrite ions per molecule of methyl picrate showed no absorption in the region 4000—6000 Å beyond that expected for *ca.* 10% residual methyl picrate. It follows that the reaction products can absorb to only an insignificant extent in that region. It also follows that nitrite formation and fading are symptoms of the same overall process, and that one nitro-group is lost per molecule in that reaction (rather than in a destructive reaction in which more

TABLE 4.

Methyl picrate. Specimen of zero-order reaction.

Time, t (min.)	3	120	231	350	446
D_t	0.838	0.772	0.700	0.632	0.569
$(D_t - D_3)/(t - 3)$ *	—	0.56	0.61	0.59	0.61

* D_3 is the optical density after 3 min.

TABLE 5.

Methyl picrate. Dependence of quantum efficiency upon sodium methoxide concentration.

[NaOMe] (M)	0.186	0.520	0.935	1.397
10%[NO ₂ ⁻] after 6 hr.	0.28	0.80	1.64	2.30
10 ¹⁰ d[NO ₂ ⁻]/dt (mole l. ⁻¹ sec. ⁻¹)	1.3	3.7	7.6	10.7
10% k	0.48	1.37	2.81	3.94
10% k /[NaOMe]	2.6	2.6	3.0	2.8

than one nitrite ion is formed). The data in Table 4 show that the reaction is of zero order with respect to the aromatic substrate over the first 30% of reaction. The result is explicable on the basis of equation (4). Most of the quanta absorbed lie in a wavelength range for which D_λ (for a cell of 2-cm. path-length) is greater than unity over the first 30% of reaction, and therefore the factor $(1 - 10^{-D_\lambda})$ remains close to unity over the same range.

In view of the zero order, the dependence of k upon the concentration of sodium methoxide was studied by measurements of the amount of nitrite formed after irradiation of solutions for 6 hr. (Table 5). Over the range of methoxide concentrations examined the concentration of the coloured 1:1 complex A remains constant (cf. Table 1 of Part I³). In the calculation of k according to equation (5), a value $S = 1.95 \times 10^{16} \text{ sec.}^{-1}$ [determined by graphical integration of equation (4) between $\lambda_1 = 3500 \text{ \AA}$ and $\lambda_2 = 5600 \text{ \AA}$] was employed.

Picric Acid.—The spectrum of picric acid in methanol showed no variation for changes in the concentration of sodium methoxide over the concentration range used in the kinetic experiments (0.052–0.52M), and corresponds to the spectrum of the picrate ion. Solutions were stable in the dark. No change in optical density was detectable for a solution of picric acid ($4.26 \times 10^{-5}\text{M}$) in 0.052M-sodium methoxide solution during 44 hr. Nitrite analyses on $21.3 \times 10^{-5}\text{M}$ -solution in 0.699M-sodium methoxide indicated the same concentration after 7 days and after

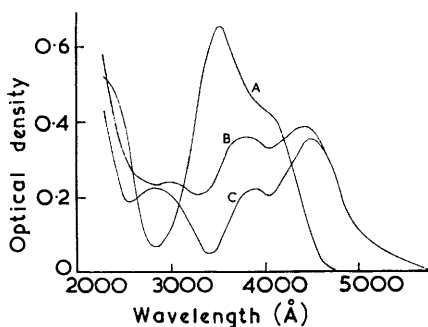


FIG. 1. Picric acid. Spectra of solutions before and after irradiation.

[Picric acid]_{stoleh} = $4.26 \times 10^{-5}\text{M}$, [NaOMe] = 0.52M.

A, initial spectrum; B, final spectrum (after 41.5 hr.); C, final spectrum less absorption due to unreacted picrate.

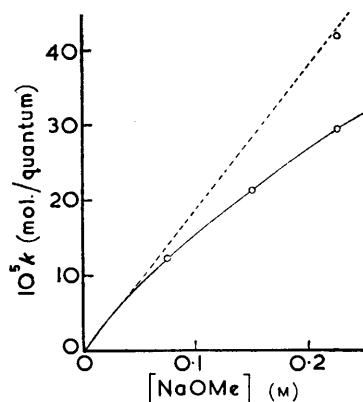


FIG. 2. Picric acid. Variation of quantum efficiency with sodium methoxide concentration (cf. Table 6).

20 days in the dark at 25°. The titres corresponded to the replacement of 0.009 nitro-group, and in view of their constancy are not considered to represent a genuine "dark" reaction but some impurity or interference in the spectrophotometric nitrite determination. Nitrite analyses and optical density measurements on irradiated $4.26 \times 10^{-5}\text{M}$ -picrate solutions indicated a definite light-reaction. In 0.52M-sodium methoxide the solution contained $3.00 \times 10^{-5}\text{M}$ nitrite after irradiation for 41.5 hr. Fig. 1 gives the spectra of the final solution and of the initial solution, and a spectrum of the product of the photochemical reaction calculated by subtracting from the final spectrum the spectrum of $1.26 \times 10^{-5}\text{M}$ picrate. The procedure rests on the assumption that, as in the reaction of methyl picrate, the photochemical change eliminates one nitro-group per picrate ion destroyed. Some measurements indicating the dependence of the rate of nitrite formation on the concentration of sodium methoxide are listed in Table 6. The final column was evaluated from equation (5) as in the case of methyl picrate,

TABLE 6.

Formation of nitrite from solutions of picric acid at varying methoxide concentrations.

[NaOMe] (M)	Time (hr.)	$10^5[\text{NO}_2^-]$ (M)	$10^{10}[\text{NO}_2^-]/t$ (mole l. ⁻¹ sec. ⁻¹)	10^5k
0.075	24	1.01	1.17	12.3
0.150	24	1.75	2.02	21.3
0.225	24	2.43	2.82	29.6
0.225	6	0.86	3.98	41.9

the graphical integration of equation (4) between $\lambda_1 = 3500$ and $\lambda_2 = 4800 \text{ \AA}$, leading to $S = 6.86 \times 10^{15} \text{ sec}^{-1}$ in this case. It seems likely that the less-than-proportional dependence of k upon $[\text{NaOMe}]$ (Fig. 2) and the falling-off in the rate of nitrite formation with time indicated by the last pair of results are both attributable to light-absorption by the reaction product (see Fig. 1). This interpretation is supported by the fact that the asymptotic slope of the graph in Fig. 2 at low methoxide concentrations passes through the experimental point at the highest methoxide concentration corresponding to the shorter reaction time, *i.e.*, there is agreement as to the value of $k/[\text{OMe}^-]$ provided that the experimental data utilised in the calculation relate to low conversions into product.

Picramide.—The loss of a nitro-group which occurs in the presence of methanolic sodium methoxide in the dark¹ is accelerated by irradiation (Table 7). The values of k were calculated on the following basis. It is assumed that the rate of the photochemical reaction can be

TABLE 7.

Picramide. Comparison of rate of nitrite formation from "dark" and "light" (irradiated) solutions.

[Picramide] _{stoich} (initial) = $3.58 \times 10^{-5} \text{M}$.			
[NaOMe] (M)	0.349	0.699	1.05
$10^5[\text{NO}_2^-]$ (M), after 24 hr. { "dark"	0.14	0.20	0.20
{ "light"	0.58	1.13	1.60
10^5k	2.83	5.98	9.01

obtained by subtracting the "dark" values from the "light" values, and that the 24-hr. points lie on zero-order reaction curves (as for methyl picrate), and accordingly the rate of nitrite formation can be deduced. The value of S , obtained by integration of equation (4) over the range $\lambda_1 = 3500$ to $\lambda_2 = 5900 \text{ \AA}$, is $1.30 \times 10^{16} \text{ sec}^{-1}$.

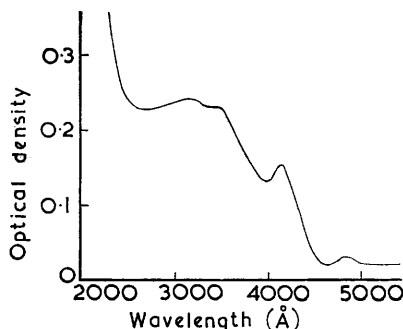


FIG. 3. Picramide. Spectrum of reaction product for irradiated solution.

[Picramide]_{stoich}(initial) = $3.03 \times 10^{-5} \text{M}$,
[NaOMe] = 1.40M.

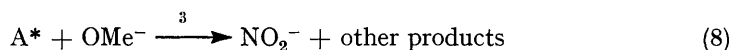
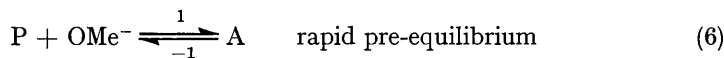
The photochemical reaction is also detectable by the more rapid variation of optical densities at 4000 and 4900 \AA for "dark" and "light" solutions. The absorption spectra of the products of the "dark" and "light" reactions are different (Fig. 3; cf. Fig. 4 of Part III¹).

DISCUSSION

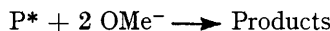
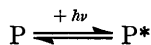
The results indicate the occurrence of a photochemical reaction by which nitrite ions are formed, in the cases of methyl picrate, picric acid, and picramide. Failure to observe the corresponding reactions with 1,3,5-trinitrobenzene and *NN*-dimethylpicramide may be due to the high velocity of the "dark" reactions of these compounds, and does not rule out the occurrence of a photochemical reaction of similar quantum yield as for the other three compounds.

For all three photochemical reactions the quantum efficiency (k) increases with increasing concentration of sodium methoxide. This result is most securely established for methyl picrate where k is proportional to $[\text{OMe}^-]$ (Table 5). The results for picric acid (Fig. 2) and picramide (Table 7) are compatible with the same conclusion. The increasing quantum efficiency is not due to increasing equilibrium conversion of substrate into a complex. For each of the three compounds the methoxide concentration range covered by these results corresponds to virtually complete conversion of the substrate into the

product of 1 : 1 interaction.^{3a,1} (The picrate ion is the 1 : 1 "complex" formed from picric acid.) This finding implies that the transition state of the photochemical reaction contains one molecule of the aromatic compound (P) and *two* methoxide ions along with a quantum of radiation. The following scheme accommodates these results:



This sequence is preferred to the scheme in which reactions (7) and (8) are replaced by the steps,



Although either scheme leads to the same reaction orders, the second one is improbable if only because P generally shows negligible light-absorption in the visible region, so that quantum efficiencies considerably in excess of unity would have to be postulated, whereas the 1 : 1 complexes absorb strongly. On this view the equilibrium constant of reaction (6) does not enter into the rate expression since, for the concentration range under discussion, the concentration of A is equal to the stoichiometric concentration of P. The rate of reaction (7) is given by the rate of light-absorption per litre of solution, *i.e.*, by

$$v_2 = S/NV$$

and the total reaction velocity by,

$$\frac{d[\text{NO}_2^-]}{dt} = \frac{k_3[\text{OMe}^-]}{k_{-2} + k_3[\text{OMe}^-]} \cdot \frac{S}{NV} \quad (9)$$

whence, by comparison with equation (5), the quantum efficiency k is given by $k_3[\text{OMe}^-]/(k_{-2} + k_3[\text{OMe}^-])$. The results for methyl picrate show direct proportionality between k and $[\text{OMe}^-]$ over a concentration range of base in which a distinction between concentration and acidity functions is not necessary. It follows that $k_{-2} \gg k_3[\text{OMe}^-]$, and the slope of the straight-line graph of k against $[\text{OMe}^-]$ should be k_3/k_{-2} . In a similar way, the asymptotic slope at low concentrations for the other two compounds should express this ratio. These results thus lead to the following values for k_3/k_{-2} : methyl picrate, 29×10^{-5} l. mole⁻¹; picric acid, 190×10^{-5} l. mole⁻¹; picramide, 8.5×10^{-5} l. mole⁻¹. Owing to difficulties in the absolute evaluation of S from equation (4), discussed in the Experimental section, the absolute values of k_3/k_{-2} are likewise subject to some uncertainty, but they are considered to be reliable for comparison purposes. The relatively low value for picramide may be anomalous if, as has been suggested,¹ "the" complex A is in this case a mixture of two species.

It is considered that nitrite ions are formed by nucleophilic displacement of a nitro-group by methoxide in the species A*. The fact that nitrite alone (rather than a mixture of nitrite and nitrate) is formed is evidence against homolytic loss of nitrogen dioxide at any stage. The organic substitution products have not been isolated or identified for any of the three compounds. We cannot rule out the possibility that the recorded product spectra (Figs. 1 and 3) correspond to compounds formed in some further (not nitrite-forming) reaction of the primary substitution product. Apart from general considerations, there is more direct evidence for the view that the nitro-group is replaced by the lyate base in the case of the photochemical reaction between hydroxide ion and 1,3,5-trinitrobenzene^{2,5} where the spectrum of the product indicates the quantitative formation of 3,5-dinitrophenol.

⁵ Gold and Rochester, *J.*, 1964, 1717.

The salient result is the requirement of the second methoxide ion in the transition state of the reaction. Only one of the compounds investigated (picramide) undergoes measurable nucleophilic displacement of a nitro-group in the dark, and for this "dark" reaction the transition state contains only a single methoxide ion. We believe that this finding throws some light on the distribution of electric charge in the excited species A^* , much as qualitative comparisons of directive effects and reactivities of aromatic molecules in their ground states can, in first approximations, be related to charge densities. (The argument can be recast in a somewhat more rigorous form in terms of the stability of transition states, but at the present stage the simpler approach seems to be more illuminating.) On this view, the displacing methoxide ion, being a nucleophilic species, will attack a site of low electron density. The fact that this attack occurs more easily in A^* than in either A or P then implies that the electronic excitation removed negative charge from the carbon atom which forms the seat of substitution to such an extent that not only does this carbon atom become more positive than in the unexcited anion A but perhaps even more positive than in the neutral molecule P. The seat of the complementary (and excess) negative charge cannot be deduced from this argument but, for the lowest excited state, we would expect it to be displaced towards or on to one or more oxygen atoms. These conclusions hold whatever view we take of the nature of A^* , *i.e.*, whether it is formed from an addition complex or by charge-transfer excitation of an outer complex. Other evidence concerning the complexes, discussed in Parts I³—III,¹ inclines us strongly towards the former view. We nevertheless wish to keep the present conclusions separate since they do not rely on the correctness of the assumed structure of A^* .

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

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