369. *The Photolysis of β-Chloro-β-nitrosobutane.*

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This paper describes the technique we have developed for measuring quantum efficiencies with red light. The value 1·2 has been obtained for the photolysis of β-chloro-β-nitrosobutane in methyl alcohol. The products, hydrogen chloride, methyl ethyl ketoxime, and the monoxime of diacetyl, have been isolated and the reaction mechanism is discussed.

Mitchell and Carson (J., 1936, 1005) showed that a mixture of β-chloro-β-nitroso- and γ-chloro-γ-nitroso-hexanes results from the photochemical action of nitrosyl chloride on *n*-hexane, and preliminary experiments indicated that the corresponding oxime hydrochlorides are produced when solutions of these chloronitroso-compounds in *n*-hexane and methyl alcohol are irradiated with red light in the absence of oxygen. We have now studied in more detail the photolysis of β-chloro-β-nitrosobutane in methyl alcohol, and have determined the quantum efficiency for red light. Hoffman (*J. Amer. Chem. Soc.*, 1934, **56**, 1894), Anderson, Crumpler, and Hammick (J., 1935, 1679), and Hammick and Lister (J., 1937, 489) have made quantum-efficiency measurements for the photolysis of some compounds containing the nitroso-group, but our technique differs considerably from theirs.

In order to simplify the energy measurements it is desirable that the light should be completely absorbed. We have found that a Christiansen filter gives light sufficiently monochromatic for this purpose, and the requisite intensity is obtained by using a carbon arc as light source. Weigert and Staude (*Z. physikal. Chem.*, 1927, **130**, 607) have shown that, when a Christiansen filter is constructed from powdered crown glass and methyl benzoate, the light which passes straight through is red at about room temperature, the other colours being scattered. By adjusting the temperature, it is possible to obtain approximately monochromatic light of any desired wave-length. We purchased a filter of this type from Schott & Gen., of Jena, and found that at 15·7° its transmission maximum, $\lambda_{max.}$, was situated at 6500 A., the wave-length of maximum absorption of a solution of β-chloro-β-nitrosobutane in methyl alcohol. Table I shows for various wave-lengths λ, the molecular extinction coefficient ε of such a solution and the percentage transmission τ_1 of the filter at 15·7°, the latter being determined by the method of Elvegard, Staude, and Weigert (*Z. physikal. Chem.*, 1929, *B*, **2**, 159). By using a red glass filter in series with the Christiansen filter, we were able to render the light more nearly monochromatic by reducing the transmission on the short-wave side of the maximum. The percentage transmission of the two filters is given by τ_2. We employed this combination in our quantum-efficiency experiments. Variations in the intensity of the arc were allowed for by reflecting a small fraction of the light on to a Weston photronic cell connected to a recording galvanometer. The same cell was used for determining the change in concentration which our solution had undergone after 7 hours of irradiation.

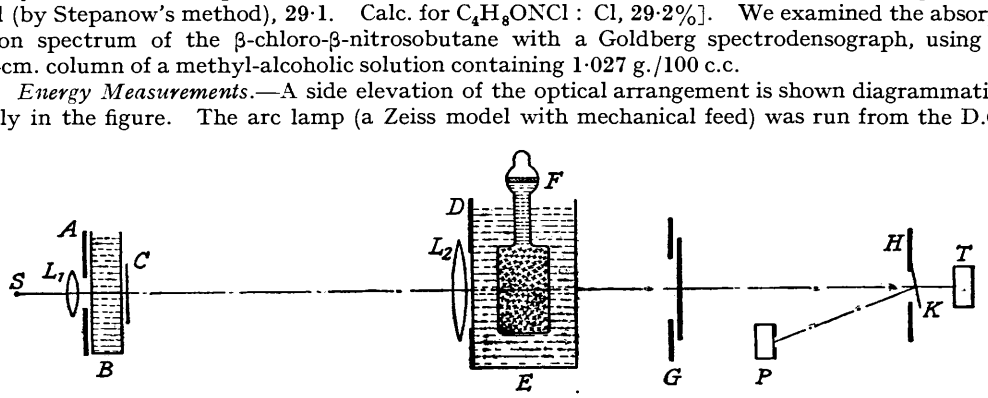
TABLE I.

λ	7000	6900	6800	6700	6600	6550	6500	6450
ϵ	5·32	6·50	8·87	11·50	14·00	14·80	15·10	14·50
τ_1	—	0·4	2·0	7·9	31·6	50·1	70·8	50·1
τ_2	—	0·4	2·0	7·9	31·6	50·1	70·8	39·8
λ	6400	6300	6200	6000	5800	5600	5400	
ϵ	13·60	11·80	10·05	7·69	5·32	2·66	0·88	
τ_1	31·6	7·9	2·0	0·2	—	—	—	
τ_2	20·0	5·0	1·0	—	—	—	—	

EXPERIMENTAL.

Preparation of β-Chloro-β-nitrosobutane.—Rheinboldt and Dewald (*Annalen*, 1927, **455**, 300) obtained this substance by the action of nitrosyl chloride on methyl *n*-butyl ketoxime, but we found that it could be prepared more conveniently by the action of chlorine on the ketoxime dissolved in dilute hydrochloric acid (cf. Piloty and Steinbock, *Ber.*, 1902, **35**, 3113). The blue oil which separated was washed with sodium carbonate solution, then with water, dried over anhydrous sodium sulphate, and distilled under reduced pressure; b. p. 35°/50 mm. [Found : Cl (by Stepanow's method), 29·1. Calc. for C_4H_8ONCl : Cl, 29·2%]. We examined the absorption spectrum of the β-chloro-β-nitrosobutane with a Goldberg spectrodensograph, using a 2-cm. column of a methyl-alcoholic solution containing 1·027 g./100 c.c.

Energy Measurements.—A side elevation of the optical arrangement is shown diagrammatically in the figure. The arc lamp (a Zeiss model with mechanical feed) was run from the D.C.



S, carbon arc; L_1, L_2, lenses of 10 and 100 cm. focal length, respectively; *A*, metal plate with rectangular aperture 2·6 × 1 cm.; *B*, circulating water-filter, 7·5 cm. thick; *C*, red glass filter (Schott & Gen., RG 2, 2 mm. thick); *D*, black paper with circular hole 8 cm. in diameter; *E*, thermostat with glass sides; *F*, Christiansen filter, 9 cm. in diameter, 4·5 cm. thick; *G*, screen with shutter; *H*, blackened screen with rectangular aperture, 2·6 × 1 cm.; *K*, glass plate inclined at a small angle to *H*; *P*, Weston photronic cell with iris diaphragm; *T*, Zeiss thermopile.

mains with a current of 8 amps., using Conradty carbons, 7 mm. positive and 5 mm. negative. A magnified image of the positive crater of the arc (about 8 cm. in diameter) was projected by L_1 through A, B, C, and D on to the front of E; L_2 formed an unmagnified image of the slit in A at the front of T. Scattered light was stopped by H, and part of the light passing through H was reflected by K on to P; H and T were mounted on an optical bench. The thermostat was kept at 15·7°.

The thermopile had an exposed surface of 2 × 0·4 cm., and it was used in conjunction with a galvanometer which gave a deflexion of 5·5 cm. on a scale at 150 cm. when the thermopile (with protecting glass removed) was exposed to the radiations from a Hefner lamp at a distance of 100 cm. Hence the energy per cm. scale division per sec., $f = (2{\cdot}25 \times 10^{-5} \times 0{\cdot}8)/5{\cdot}5$ cals. $= 3{\cdot}273 \times 10^{-6}$ cals. (cf. Gerlach, *Physikal. Z.*, 1913, **14**, 577).

The photocell was connected to a recording galvanometer, and the iris diaphragm in front of the cell was adjusted so that the ratio of the deflexion produced by the thermopile (protected by the glass plate) to that produced by the photocell was about 6 to 1. A series of photographs were then taken with the shutter G alternately opened and closed for 30 secs., the corresponding readings produced by the thermopile being noted in each case. Some typical results are in Table II. From these it is seen that the ratio of thermopile reading T to the mean photocell reading P is practically constant, so that the deflexion given by the photocell can be taken as proportional to the light intensity for the range with which we are concerned in our experiments. The average value for T/P (which we shall denote by a_1) is equal to 6·37.

A rectangular glass cell, 1 cm. thick and having a ground glass stopper, was then filled with 2·7 c.c. of a solution of 4·001 g. of β-chloro-β-nitrosobutane in 100 c.c. of methyl alcohol, which had been freed as far as possible from dissolved oxygen by bubbling in nitrogen and then distilling it in an atmosphere of nitrogen. The thermopile was moved back a short distance, and the glass cell was inserted in front of it in a holder having a slit 2 × 0·4 cm., so that this slit was in the position previously occupied by the slit of the thermopile. The solution was then irradiated for 7 hours. For this period 7 pairs of carbons, each burning for 1 hour, were required. A photographic record of the variations in the intensity of the light was made for each pair of carbons, and the mean photocell deflexion P' was found from each record. Table III gives the results obtained. The average of the P' values (which we shall call a_2) is 9·3 cm. Introducing a correction of 5% for light losses by reflection, and denoting the time of irradiation in secs. by t, we calculate that the total energy absorbed $= f \times 1{\cdot}05a_1 \times a_2 \times t = 5{\cdot}142$ cals.

TABLE II.

T (cm.)	61·5	58·8	61·4	61·4	55·0	59·4	60·7	59·9	59·0
P (cm.)	9·7	9·3	9·5	9·6	8·5	9·4	9·6	9·2	9·2
T/P	6·34	6·32	6·46	6·40	6·46	6·31	6·32	6·35	6·41

TABLE III.

Carbons	1	2	3	4	5	6	7
P' (cm.)	9·2	8·9	9·4	9·7	9·6	9·0	9·3

Mols. decomposed.—For measuring the concentration at the end of the period of irradiation, the arrangement in the figure was slightly modified. An Osram 12-volt, 100-watt projection lamp run from accumulators was substituted for the carbon arc, and the thermopile was replaced by the photocell. This light source was found to be steady to 1 part in 500. 2 C.c. of the partly decomposed solution from the cell were made up to 10 c.c. with methyl alcohol. This diluted solution was then placed in a glass cell 1 cm. thick fixed in front of the photocell, and the deflexion was noted. Readings were also taken with the cell filled with solutions of β-chloro-β-nitrosobutane in methyl alcohol of the concentrations shown in Table IV. The concentration x of the irradiated solution (5 times diluted) was then found graphically to be 0·6702 g./100 c.c. of solution. Hence, mols. decomposed $= [2{\cdot}7 \times (4{\cdot}001 - 3{\cdot}351)]/(100 \times 121{\cdot}5) = 1{\cdot}444 \times 10^{-4}$.

TABLE IV.

Concn., g./100 c.c. of soln.	0·8002	0·7202	0·6402	0·5601	x
Deflexion (cm.)	16·9	20·7	25·4	31·1	23·6

Quantum Efficiency.—The quantum efficiency γ is given by

$$\gamma = [(\text{mols. decomposed})/(\text{cals. absorbed})] \times [(2{\cdot}847 \times 10^7)/650] = 1{\cdot}2$$

(cf. Allmand, *Trans. Faraday Soc.*, 1925—26, **21**, 442). Another experiment carried out with a 6% solution of β-chloro-β-nitrosobutane in methyl alcohol also gave $\gamma = 1{\cdot}2$.

Effect of Concentration on the Quantum Efficiency.—The effect of concentration was investigated by carrying out two experiments in duplicate. For these, two pairs of cells were made from glass tubing of 2·5 cm. internal diameter and severally 1 and 2 cm. long. The cells were closed by glass discs cemented in position. Each cell had a narrow side tube into which a tightly fitting glass rod was fitted and held with a short piece of rubber tubing. In the first experiment, the 1 cm. cells were filled with an 8% solution of β-chloro-β-nitrosobutane in methyl alcohol, and the 2 cm. cells with a 4% solution. The cells were mounted close together on a wooden stand so that their centres lay on the circumference of a circle and the two sizes alternated. They were then exposed for 4 hours to a beam of sunlight which had passed through a water-filter and a red glass filter, an improvised heliostat ensuring that the beam was always parallel to the cell walls. Considerable photolysis had then taken place, and the solutions were diluted (the first by twice as much as the second) and examined in the photoelectric colorimeter already described. All were found to be decomposed to the same extent. The same result was obtained in the second experiment when the 1 cm. cells were filled with 4% solution, the 2 cm. cells with 2% solution, and the irradiation was carried on for 2 hours. We can conclude from these experiments that the quantum efficiency does not change with concentration within the limits 2—8%.

Products of Photolysis.—For most of our work an approximately 5% solution of β-chloro-β-nitrosobutane in methyl alcohol was used. This solution was stable when kept in the dark, but when it was exposed to red light the blue colour gradually faded and the solution became practically colourless. If the solution was open to the air during irradiation, part of the β-chloro-β-nitrosobutane was oxidised to the nitro-compound, so we carried out our experiments in sealed tubes in order to eliminate this complication. The tubes were placed in a glass vessel through which water circulated, and were exposed either to sunlight or to the light from ordinary electric lamps. After photolysis, the solution was found to contain hydrogen chloride, which was estimated by titration with standard silver nitrate solution. 2 C.c. of a solution which before photolysis contained 4·904 g. of β-chloro-β-nitrosobutane in 100 c.c. of solution required 8·1 c.c. of 0·09458N-silver nitrate, so that after photolysis 95% of the total chlorine was present as chloride ion. From another portion of the solution, which had been rendered practically colourless by irradiation, the methyl alcohol was removed at room temperature under reduced pressure and a brown, partly solid residue was obtained. This was dissolved in a little water, and the resulting solution neutralised with potassium hydroxide and then extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and filtered and after removal of the ether the remaining oil was distilled under reduced pressure. A colourless liquid (I), b. p. 50°/6 mm., was obtained, together with a small amount of a white solid (II), m. p. 74·5°, which collected in the upper part of the condenser. Some tarry material left in the flask was not further examined. The aqueous solution from which these products had been extracted was evaporated to dryness under reduced pressure, and the solid residue extracted with ether (Soxhlet). When this extract was concentrated, a white solid (III) separated, m. p. 55°. From 55 g. of β-chloro-β-nitrosobutane the following quantities of the various products were obtained: (I), 7 g.; (II), 1 g.; (III), 16 g.; hydrogen chloride, 15·7 g.

The liquid (I) was identified as methyl ethyl ketoxime from the following data: $n_D^{20°}$ 1·4402 (an authentic specimen had $n_D^{20°}$ 1·4410); steam-distillation after the addition of some hydrochloric acid gave a ketone whose semicarbazone had m. p. 143° (mixed with this and alone, the semicarbazone from methyl ethyl ketone had the same m. p.). The solid (II) was identified as diacetyl monoxime (Found: C, 47·5; H, 6·7; N, 14·0. Calc. for $C_4H_7O_2N$: C, 47·5; H, 6·9; N, 13·9%) and had m. p. 74·5°. Treatment with hydroxylamine hydrochloride produced dimethylglyoxime, which formed the characteristic nickel compound. On analysis, (III) gave C, 51·3; H, 8·5; N, 15·2; *M*, cryoscopic in benzene, 235; ebullioscopic in alcohol (Menzies's method), 188 ($C_8H_{16}O_3N_2$ requires C, 51·1; H, 8·5; N, 14·9%; *M*, 188). The number of hydroxyl groups in (III) was determined by the method of Zerewitinoff (*Ber.*, 1907, **40**, 2023)). Pyridine was used as solvent and 0·0990 g. of the substance gave 38·90 c.c. of methane at 20° and 760 mm., which corresponds to 3 hydroxyl groups per molecule. When (III) was allowed to stand with methyl-alcoholic hydrogen chloride, and the solution was then treated in the same way as that obtained in the photolysis of the β-chloro-β-nitrosobutane, (I) and (II) were isolated in about equal quantity. The compound (III) is therefore regarded as *γ-hydroxy-γδ-dimethylhexan-βε-dione dioxime.*

An attempt was then made to purify the brown, partly solid residue (see above). When it

was washed with methyl acetate, a slightly brown solid remained which, after crystallisation from benzene, was white. This product (IV) absorbed moisture on exposure to the air and soon became coloured, but it was stable when kept over calcium chloride in a vacuum desiccator. It started to melt at 110° (decomp.) (Found: N, 13·6; Cl, 17·0. $C_8H_{14}O_2N_2$,HCl requires N, 13·6; Cl, 17·2%. The same result was obtained for Cl by Stepanow's method and by titration with standard silver nitrate). When an aqueous solution of (IV) was neutralised with potassium hydroxide, evaporated to dryness, and the residue was extracted with ether, product (III) was obtained, so that (IV) can be regarded as the parent of (III). The substance (IV) is presumably the *monohydrochloride* of *γδ-dimethyl-Δ$^{\gamma}$-hexadiene-βε-dione dioxime* (IV').

Other Solvents.—The photolysis of β-chloro-β-nitrosobutane was also investigated in acetone, carbon tetrachloride, and *n*-hexane as solvents. With acetone the solution remained homogeneous as with methyl alcohol, but with carbon tetrachloride and *n*-hexane the products of photolysis separated as yellow oils which became brown on standing. These oils contained considerable amounts of tarry material, which rendered difficult the isolation of the reaction products. We were able, however, to show the presence of hydrogen chloride, (I), (II), and (III) in every case.

Conclusion.

The value $\gamma = 1{\cdot}2$ has been obtained for the photolysis of 4 and 6% solutions of β-chloro-β-nitrosobutane in methyl alcohol, and additional experiments have shown that the quantum efficiency is independent of concentration for the range 2—8%. The following mechanism is suggested:

$$NO{\cdot}CMeCl{\cdot}CH_2Me + h\nu \longrightarrow \underbrace{[C_4H_7ON]}_{\text{unsaturated residue}} + HCl$$

$$2[C_4H_7ON] \longrightarrow \underbrace{\begin{matrix} HO{\cdot}N{:}CMe{\cdot}CMe \\ \| \\ HO{\cdot}N{:}CMe{\cdot}CMe \end{matrix}}_{\text{(IV'.)}} \xrightarrow{H_2O} \underbrace{\begin{matrix} HO{\cdot}N{:}CMe{\cdot}CHMe \\ | \\ HO{\cdot}N{:}CMe{\cdot}CMe{\cdot}OH \end{matrix}}_{\text{(III.)}} \longrightarrow \begin{matrix} HO{\cdot}N{:}CMe{\cdot}CH_2Me \quad \text{(I.)} \\ + \\ HO{\cdot}N{:}CMe{\cdot}COMe \quad \text{(II.)} \end{matrix}$$

Hammick and his collaborators (*loc. cit.*) have shown that when certain aliphatic nitroso-compounds are irradiated with red light the group NOH is split off. With the chloronitroso-compound now investigated, the more negative chlorine atom is removed along with hydrogen in preference to the nitroso-group. Further work on the photochemistry of chloronitroso-compounds is in progress.

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