399. *The Photochemical Decomposition of Nitroso*iso*propylacetone and β-Nitroso-βε-dimethylhexane.*

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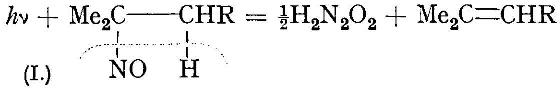
The effect of light on solutions of nitroso*iso*propylacetone and other aliphatic nitroso-compounds was examined by Bamberger (*Ber.*, 1903, **36**, 685), who observed that when two identical solutions of the colourless bimolecular forms were kept, one in the dark and the other in sunlight, the rate of development of the blue colour due to the unimolecular form was slower in the light than in the dark. From this he concluded that light exerted a retarding influence on the rate of depolymerisation. Preliminary experiments, already referred to (this vol., p. 30), showed, however, that Bamberger's conclusions are erroneous, and that the phenomena he observed are due to decomposition of the blue unimolecular form by light at a rate greater than that at which it is produced by depolymerisation.

We now describe the photochemical decomposition in greater detail. We find that each of the substances specified in the title is decomposed by light with a photochemical equivalence of 1 mol. per quantum of light absorbed. We also find that in each case hyponitrous acid and its decomposition products are formed, together with mesityl oxide from the nitroso-ketone (I; R = COMe), and an unsaturated hydrocarbon, probably a βε-dimethylhexene, from the nitroso-hydrocarbon (I; R = CH_2·$CHMe_2$), in accordance with the equation



$$h\nu + \underset{\mathrm{NO}}{\mathrm{Me_2C}}\text{——}\underset{\mathrm{H}}{\mathrm{CHR}} = \tfrac{1}{2}H_2N_2O_2 + Me_2C{=}CHR$$

(I.)

EXPERIMENTAL.

Materials.—Nitroso*iso*propylacetone was prepared by oxidation of diacetonamine oxalate (Everest, J., 1919, **115**, 588) with Caro's acid by Bamberger's method (*loc. cit.*); m. p. 75·5°. A small quantity (0·3 g.) of β-nitroso-βε-dimethylhexane, prepared by Dr. R. G. A. New (J., 1932, 742), was available; m. p. 53—54°. The photochemical decomposition of these substances was studied in solution in carefully purified benzene; m. p. 5·4°.

Absorption Spectra.—The absorption spectrum of unimolecular nitroso*iso*propylacetone has already been recorded (this vol., p. 30). For the other compound the following data were obtained; *D* represents the colour density for wave-length λ at concentration *C* (g.-mols./l.; benzene solution); *l* = 1·95 cm.

C = 0·035.

λ.	*D.*	λ.	*D.*	λ.	*D.*
7400	0·486	6950	1·635	6550	1·267
7300	0·740	6900	1·685	6500	1·211
7250	0·895	6850	1·700	6400	0·997
7200	1·047	6800	1·665	6300	0·847
7150	1·208	6750	1·614	6200	0·664
7100	1·345	6700	1·565	6100	0·587
7050	1·500	6650	1·473	6000	0·440
7000	1·552	6600	1·385	5800	0·260

C= 0·024.

λ.	*D.*	λ.	*D.*	λ.	*D.*
7400	0·255	6800	1·105	6200	0·502
7300	0·478	6700	1·050	6100	0·429
7200	0·644	6600	0·935	6000	0·301
7100	0·854	6500	0·815	5900	0·255
7000	1·000	6400	0·702	5800	0·182
6900	1·125	6300	0·587		

Graphs of *D* against λ show that for each concentration maximum absorption occurs at λ = 6850 Å., which is 150 Å. further into the red than the maximum for nitroso*iso*propylacetone.

Apparatus.—Apparently, no colour filters are known that will transmit homogeneous light at wave-lengths within the range of those absorbed by the two nitroso-compounds. Filters were, however, constructed that transmitted a band of red light between 6400 and 7100 Å. A parallel beam of light from a 500-watt tungsten lamp was passed first through 6·5 cm. of a solution containing 40 g. of nickel chloride, 110 g. of ferrous ammonium sulphate, and 15 c.c. of concentrated hydrochloric acid in a litre of water. The amount of infra-red radiation transmitted by this filter was found to be negligible. A second filter, 5·2 cm. thick, contained a solution of Congo-blue BX and chrysoidine at concentrations of about 1 part in 6,000 and 10,000 parts respectively. The absorption data for the two filter solutions, measured at a thickness of 4 cm., are given below :

λ.	*D* (Dye filter).	*D* ($NiCl_2$).	λ.	*D* (Dye filter).	*D* ($NiCl_2$).
7200	0·370	1·355	6700	1·255	1·145
7100	0·425	1·335	6600	1·655	1·120
7000	0·485	1·315	6500	2·225	1·120
6900	0·630	1·285	6400	2·975	1·120
6800	0·875	1·225	6300	—	1·120

Over 90% of the incident light is absorbed by these filters in series, and they are of use only because the photodecompositions of the nitroso-compounds are rapid. The actual amount of energy transmitted to the reaction cell, when the lamp was full on, was of the order of 20 × 10^{-4} cal./sec.

After passing through the filters, the light was directed by means of a long-focus lens through a circular aperture 1 cm. in diameter in a Uralite screen into the reaction cell.

Kinetics of the Photodecompositions.—The rate of disappearance of the blue nitroso-compounds under the influence of light was followed by means of colour-density determinations with a Hilger–Nutting spectrophotometer, using light of λ 6000 Å. At this wave-length the relation between D and C for unimolecular nitroso*iso*propylacetone is linear, and for $l = 1{\cdot}95$ cm. is given by $C = 0{\cdot}0556D$. This relation is derived from the following data :

C	0·0275	0·0575	0·0814	0·1042
D (6000 Å.)	0·501	1·032	1·465	1·830
C/D	0·0548	0·0557	0·0556	0·0569

Data showing that for complete absorption the rate of photochemical reaction in benzene solution is proportional to the light intensity and independent of the concentration of nitroso*iso*propylacetone are given in Table I. They were obtained with a solution of the nitroso-compound that had been kept in the dark for 12 hours, to ensure complete depolymerisation (cf. Bamberger, *loc. cit.*), and contained initially 0·085 g.-mol./l. of unimolecular form. During Run II, a piece of wire gauze was placed between the filter system and the absorption tube containing the solution of nitroso-compound. By means of a standardised thermopile the gauze had previously been shown to transmit 38% of the incident light. The absorption tube ($l = 1{\cdot}95$ cm.) was shaken at frequent intervals during the runs, and protected from light during its transference to and from the spectrophotometer. Each value of D, as in all measurements of colour density, is a mean of at least six readings.

TABLE I.

Run I. No gauze.							
Time (mins.)	0	25	50	75	100	125	175
D (6000 Å.)	1·543	1·523	1·507	1·490	1·474	1·455	1·421
Run II. Gauze present.							
Time (mins.)	0	75	150	225	300	375	
D (6000 Å.)	1·543	1·523	1·498	1·482	1·456	1·438	

The plots of the two sets of time–colour density data are straight lines, given by $D_1 = 1{\cdot}543 - 0{\cdot}0007t_1$ and $D_2 = 1{\cdot}543 - 0{\cdot}00028t_2$ respectively, and show that the reaction is of zero order. The ratio of the slopes of the two lines (II/I) is 0·40; the ratio of the light intensities being 0·38, the rate of reaction is thus very nearly proportional to the first power of the light intensity. Each run was continued with frequent shaking until about 10% transformation had occurred, at which it was found that more than 99% of the light entering the reaction cell was still being absorbed.

Quantum Efficiency.—For the determination of the quantum efficiency of the photodecomposition of nitroso*iso*propylacetone, the absorption tube previously used was replaced by a flat quartz cell of thickness 1·0 cm. and diameter 5 cm. in order to minimise absorption of radiation by the sides. For this cell the relation between colour density and concentration was $C = 0{\cdot}0556 \times D \times 1{\cdot}95 = 0{\cdot}1084D$ (see above). A solution (15 c.c.) containing 0·130 g.-mol./l. was illuminated as before with light of λ 6400—7100 Å. for 13 hours, the value of D_{6000} falling from 1·226 to 1·035. This corresponds to the disappearance of $3{\cdot}10 \times 10^{-4}$ g.-mol. of nitroso*iso*propylacetone. During this experiment the light entering the cell was not completely absorbed, and the amount actually absorbed during the run was found by a difference method. The reading on a standardised thermopile was noted when the instrument was placed behind the cell containing pure solvent (benzene). Readings were also taken at the beginning and at the end of the run. The difference between the mean of these readings and the value when solvent alone was in the cell gave $3{\cdot}21 \times 10^{-4}$ quanta at 6700 Å. absorbed during the 13-hours run. The quantum efficiency of the reaction is thus unity within the limits of experimental accuracy.

β-*Nitroso*-βε-*dimethylhexane.*—Owing to the small amount of this substance available, it was not possible to examine the kinetics of its photodecomposition under conditions of complete light absorption. We therefore proceeded as follows. Benzene solutions of nitroso*iso*propylacetone (0·046M) and β-nitroso-βε-dimethylhexane (0·0315M) were kept for 12 hours to ensure complete dissociation to the unimolecular forms. Each solution was then exposed, in the 1·95-cm. tube, to light that had passed through a ferrous ammonium sulphate filter (90 g. in 300 c.c. of water and 15 c.c. of concentrated sulphuric acid) and a piece of red glass known to transmit the lines 6700 Å. and 6850 Å., which correspond to the maximum absorptions of the two compounds, with approximately the same efficiency. Colour-density determinations were in each case made every 10 minutes, at λ 6700 and 6850 Å. respectively. Results are given in Table II.

TABLE II.

Nitroso*iso*propylacetone.			β-Nitroso-βε-dimethylhexane.		
Time (mins.).	D_{6700}.	k_1.	Time (mins.).	D_{6850}.	k_2.
0	1·937	—	0	1·520	—
10	1·695	0·013	10	1·300	0·016
20	1·509	0·013	20	1·129	0·015
30	1·303	0·013	30	0·985	0·014
40	1·122	0·014	40	0·844	0·015
50	0·936	0·014	50	0·708	0·015
60	0·802	0·015	60	0·608	0·015

For incomplete absorption the rate of photodecomposition should in each case be proportional to the amount of light absorbed, and hence to the colour density D; k_1 and k_2 are the unimolecular constants calculated from the corresponding values of D. It has been shown that the photodecomposition of nitroso*iso*propylacetone has a quantum efficiency of unity, and the light intensities at the maximum absorption for each solution were approximately the same. From the approximate equality of the velocity constants, we can therefore conclude that the photodecomposition of the nitrosodimethylhexane has nearly the same quantum efficiency as that of the nitroso-ketone.

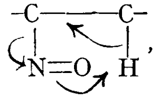
The same conclusion can be derived from the results in a different way. The mean light absorption by the ketone solution (3·33 c.c. of 0·046M) over the first 50 minutes of change was 94·9%, which is also the mean absorption for the nitroso-hydrocarbon solution (3·33 c.c. of 0·0315M) over the first 20 minutes. From the fractional change in colour density of the former solution we find that $1·48 \times 10^{-6}$ quantum at 6700 Å. is absorbed per minute. Assuming that energy is absorbed at the same rate during the first 20 minutes of illumination of the latter solution, we find that the number of quanta at 6850 Å. (maximum absorption) in 20 minutes is $2·89 \times 10^{-5}$. From the fractional change in the colour density, the number of g.-mols. decomposed in 20 minutes is found to be $2·7 \times 10^{-5}$.

Products of the Photochemical Decompositions.—A benzene solution of nitroso*iso*propylacetone that had been exposed to light until it was colourless was found to contain mesityl oxide, identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 192°. Repeated tests showed that no combined nitrogen remained in the solution. The effect of light has thus been to remove the group NOH from the nitroso-compound. The removal of the group as such might be expected to result in the production of hyponitrous acid and its decomposition products, and, in fact, the aqueous extract of the benzene solution gave with silver nitrate the characteristic yellow precipitate of silver hyponitrite, soluble in acids and reprecipitated by ammonia. Moreover, during the illumination of the nitroso-solution in a gas burette, a gas was evolved which showed no contraction on treatment with water, oleum, caustic potash, or a faintly alkaline solution of sodium sulphite, which is an efficient absorbent for nitric oxide (Divers, J., 1899, **75**, 82). No change occurred on sparking with hydrogen or oxygen, and the gas was therefore pure nitrogen. A similar evolution of nitrogen was observed by Mitchell (J., 1930, 1829) as a product of the photodecomposition of humulene nitrosite by red light.

It has been shown by Ray and Ganguli (J., 1907, **91**, 1866) that hyponitrous acid can decompose in accordance with the equation $5H_2N_2O_2 = 2HNO_3 + 4N_2 + 4H_2O$ in the presence of acid, which probably means that, as hyponitrous acid is a weak acid, it is a reaction of the un-ionised molecules. In benzene solution ionisation is certain to be extremely small and the production of nitrogen and nitric acid is to be expected. Nitric acid was, in fact, found to be present. Nitrous acid was also present in the aqueous extract, and is presumably the source of the small quantity of nitric oxide evolved when pressure in the gas-burette is lowered after evolution of nitrogen has ceased (cf. Taylor, Wignall, and Cowley, J., 1927, 1923). Nitrous acid has been identified as a product of the decomposition of hyponitrous acid by Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 317), and a possible equation for its formation is $3H_2N_2O_2 = 2HNO_2 + 2N_2 + 2H_2O$. The volume of nitrogen evolved during the photodecomposition of 0·1 g. of nitroso*iso*propylacetone in benzene solution was therefore measured and found to be 4·5 c.c. at *N.T.P.* (mean of three experiments). Simultaneous decomposition by the two processes represented by the above equations ($8H_2N_2O_2 \longrightarrow 6N_2$) would yield 6·5 c.c. at *N.T.P.*

The photodecomposition in benzene solution of β-nitroso-βε-dimethylhexane was found to give the same products, except that, instead of mesityl oxide, there was found in solution a nitrogen-free unsaturated liquid, which reacted with bromine in carbon tetrachloride without substitution and is presumably βε-dimethyl-Δ^{β}-hexene, $CMe_2{:}CH{\cdot}CH_2{\cdot}CMe_2$. Owing to the small amount of material available, this hydrocarbon could not be isolated and characterised.

DISCUSSION.

The above view that the photochemical decomposition of nitroso*iso*propylacetone depends on the primary elimination of the radical NOH is in agreement with the nature of the decomposition products found (mesityl oxide, and hyponitrous acid and its decomposition products). Although the experimental data for β-nitroso-βε-dimethylhexane are not so complete, sufficient evidence has been obtained to make it probable that it decomposes in an analogous way. In each case the photochemical decomposition has an efficiency of 1 mol. per quantum of light absorbed, and it is therefore possible to compare the quantity of energy known to be absorbed per mol. of nitroso-compound with the energy required to bring about the change formulated on p. 1680. The electronic processes involved in the splitting off of NOH are  , and are seen to consist in the rupture of the linkages –C—H, –C—N–, and ½N═O, and the formation of –C═C– from –C—C– and of –O—H. In estimating the energy associated with making and breaking these links, we have taken Sidgwick's values (" The Co-valent Link in Chemistry," 1933, p. 119) for C═C from C—C, C—H, and O—H. Following him, we have assumed that the heat of formation of the double link N═O is twice that of the single link N—O, but have recalculated its value from the heat of combustion of ethyl nitrite, *viz.*, 332·6 kg.-cals. (Kharasch, *Bur. Stand. J. Res.*, 1929, 2, 339), using the mean, 168·8 kg.-cals., of the two recent determinations of the heat of atomisation of nitrogen (Mulliken, *Physical Rev.*, 1934, **46**, 144 : 168·3 kg.-cals.; Herzberg and Sponer, *Z. physikal. Chem.*, 1934, *B*, **26**, 1 : 169·3 kg.-cals.). Taking Sidgwick's values for 5 C—H links, C—C, and C—O, we find 114·28 kg.-cals. for N═O, and hence 57·14 kg.-cals. for N—O. A similar recalculation of the heat of formation of the link C—N from the heats of combustion of methylamine and dimethylamine (259 and 422 kg.-cals. respectively; Kharasch, *loc. cit.*) yields the value 53·79 kg.-cals. From these and Sidgwick's values for the heats involved in the rupture and formation of the linkages that occur in the process given above for the elimination of the group NOH, we find that an absorption of 42·68 kg.-cals. per g.-mol. is required, with an uncertainty of possibly ± 5%.

The energy absorbed by 1 g.-mol. of nitroso*iso*propylacetone with an efficiency of 1 quantum per mol. at the wave-length 6700 Å., corresponding to maximum absorption, is 42·26 kg.-cals. For the nitroso-hydrocarbon the corresponding value (at 6850 Å.) is 0·93 kg.-cal. less. We can therefore conclude that the light energy absorbed by these two nitroso-compounds is sufficient to meet the energy requirement, 40—45 kg.-cals.,* of the photochemical decomposition postulated.

The close agreement between the light energy absorbed and that required for decomposition is doubtless fortuitous. The group –C—N═O is characterised by its ability to absorb red light, and in the two compounds concerned the energy thus absorbed is just sufficient to bring about the elimination of the group NOH. It is unlikely that the condition for absorption is the ability to undergo this kind of photodecomposition, for other nitroso-compounds, *e.g.*, the nitrosobenzenes, absorb red light without decomposing in the same way or at anything like the same rate.

SUMMARY.

Nitroso*iso*propylacetone and β-nitroso-βε-dimethylhexane are decomposed by red light with unit quantum efficiency to give respectively mesityl oxide and, most probably,

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* On the basis of the earlier value (208 kg.-cals.; Sidgwick, *op. cit.*) for the heat of atomisation of the nitrogen molecule, the energy requirement would be 53·6 kg.-cals., which would necessitate absorption of quanta at 5280 Å. for photochemical decomposition. At this wave-length practically no light is absorbed by benzene solutions of either of the nitroso-compounds.

βε-dimethyl-Δ^{β}-hexene. In each case hyponitrous acid and its decomposition products are produced. The light energy absorbed is shown to be sufficient to supply the energy required to eliminate the group NOH from the molecules of the two nitroso-compounds.

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