# 348. *Primary Photochemical Processes. Part IX. A Preliminary Study of the Decomposition of Nitromethane and Nitroethane.*

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APPARENTLY no observations have been recorded relating to the photochemistry of simple nitro-compounds. We have therefore made a preliminary study of the photochemical decomposition of nitro-methane and -ethane with a view to establish the nature of the primary photochemical change in this class of compound. The absorption spectra of these two substances as liquids have been investigated by Baly and Desch (J., 1908, **93**, 1747), Purvis (J., 1913, **103**, 1088), Hantzsch (*Ber.*, 1912, **45**, 85; *Z. Elektrochem.*, 1912, **18**, 470), and Zelinsky (*J. pr. Chem.*, 1912, **78**, 692), all of whom characterise two regions of continuous absorption, the first with its maximum at about 3000 A., and the second starting at 2500 A., and extending towards the shorter ultra-violet. While this work was in progress, Goodeve (*Trans. Faraday Soc.*, 1934, **30**, 504) measured the photometric extinction curves of nitroethane, which was found to have a continuous absorption in the gaseous state from 3225 A. towards the ultra-violet, and she concluded that the molecule dissociates completely on absorption of light. Later, Thompson and Parker (*Trans. Faraday Soc.*, 1936, **32**, 674) described the absorption spectra of the vapours of nitromethane and nitroethane, and our observations are in general agreement with theirs; absorption starts at 3040 A. for the former and at 2920 A. for the latter. In both cases the main absorption is continuous to beyond 1800 with subsidiary minima at *ca.* 2450 and *ca.* 2400 A. respectively; we have, however, found evidence of faint diffuse structure in the early part of the nitroethane absorption region at 3000 A.*

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* Besides continuous absorption, we have also found in this compound some superimposed fine structure. In our photographs there appear four pairs of lines, a stronger with a weaker companion 10 A. apart in the long wave-length side, and numerous weaker lines between and afterwards. This structure is not described by any of the other authors. It is possible that the banded absorption is due to some impurity, but it appears in the compounds of B.D.H. origin as well as in those prepared in the laboratory. The b. p. measurements gave exact agreement. The alkyl iodide used in the preparation has only continuous absorption in this spectral region. With the spectrum of benzene, which is always a possible impurity, there is no agreement within the limits of accuracy. The question as to the origin of the fine structure has therefore to remain open. It is impossible to analyse the spectra; they are very complex and are not fully resolved under the dispersion used.

By analysis of the decomposition products we have been able to characterise the primary photochemical change as an elimination of the oximino-group, leaving an aldehyde, which was readily detected: $CH_2R\cdot NO_2 = CHR{:}O + NOH$. The subsequent secondary reactions of the free radical account quantitatively for the other products obtained. This reaction forms an interesting analogy with that of Anderson, Crumpler, and Hammick (J., 1935, 1679), who recently established a similar photochemical elimination of the oximino-radical from certain nitroso-compounds.

## EXPERIMENTAL.

The study of photochemical decomposition of the vapours was carried out in an apparatus similar to that used with aldehydes and ketones (Norrish and Appleyard, J., 1934, 875), in which the liquid, screened from the light, is kept refluxing in a long-necked quartz flask, and the vapour in the neck is irradiated by a vertical mercury lamp placed in a parallel position. The products of decomposition collect in a large evacuated globe out of the region of illumination. As judged from the absorption spectrum of the nitro-compounds and the distribution of energy in the mercury spectrum, the wave-lengths responsible for the photodecomposition in the present case lay between 2000 and 3000 A.

The compounds used were prepared from the corresponding alkyl iodides and silver nitrate in the usual manner. Commercial specimens were also employed. In all cases they were distilled in a vacuum, and their purity finally checked by b. p. measurements.

During irradiation, there was a steady increase of pressure. After about 50 hours the products were pumped off in two fractions, (*a*) at liquid-air temperature (− 180°) and (*b*) at the temperature of carbon dioxide and ether (− 80°); these were analysed separately in a Bone and Wheeler apparatus. The following results were obtained, the volumes being given in c.c. at *N.T.P.*

*Nitromethane.* Expt. I (58 hours' irradiation).

| | Total vol. | $N_2$. | CO. | NO. | $CO_2$. | Residue. |
|---|---|---|---|---|---|---|
| Fraction (*a*) | 28·1 | 14·9 | 5·7 | 7·5 | — | — |
| Fraction (*b*) | 6·7 | — | — | 3·3 | 2·2 | 2·2 |
| Total | 34·8 | 14·9 | 5·7 | 10·8 | 2·2 | 2·2 |

Expt. II (62 hours' irradiation).

| | Total vol. | $N_2$. | CO. | NO. | $CO_2$. | Residue. |
|---|---|---|---|---|---|---|
| Fraction (*a*) | 20·1 | 13·5 | 2·8 | 3·8 | — | — |
| Fraction (*b*) | 12·9 | — | — | 7·5 | 3·2 | 2·2 |
| Total | 33·0 | 13·5 | 2·8 | 11·3 | 3·2 | 2·2 |

*Nitroethane* (67 hours' irradiation).

| | Total vol. | $N_2$. | CO. | NO. | $NO_2$. | $CO_2$. | Unsatd. hydrocarbons. | Residue. |
|---|---|---|---|---|---|---|---|---|
| Fraction (*a*) | 15·5 | 9·1 | 4·8 | 1·6 | — | — | — | — |
| Fraction (*b*) | 19·9 | — | — | 5·9 | | 1·8 | 9·6 | 2·6 |
| Total | 35·4 | 9·1 | 4·8 | 7·5 | | 1·8 | 9·6 | 2·6 |

The chief difference in the products from the two compounds lies in the large quantity of unsaturated hydrocarbon produced from nitroethane, and also in the fact that a considerable quantity of nitrogen dioxide was present in fraction (*b*). In the gas analysis no distinction had been made between nitric oxide and the dioxide.

In a second experiment with nitroethane, after the gas fraction uncondensable in liquid air had been pumped off, the residue volatile at − 120° was collected. This proved to contain nitric oxide and all the unsaturated fraction. This sample was introduced into a Bone and Wheeler apparatus and shaken with an alkaline solution of sodium sulphite the special function of which was to remove nitric oxide as $Na_2SO_3,2NO$ and also any trace of the dioxide and of carbon dioxide. One sample of the residue was found to be absorbed by bromine water to the extent of 98%, and another exploded with oxygen and gave a contraction of 1·97 vols. and produced 1·96 vols. of carbon dioxide. In this way the unsaturated hydrocarbon was identified as ethylene.

In using these results to obtain a carbon balance, we have assumed that the whole of the nitrogen of the decomposed nitro-compound appears in the gas phase as nitrogen or its monoxide or dioxide. This assumption is justified finally by the simplicity of the result. Working in this way, we calculate the deficiency of carbon, oxygen, and hydrogen among the gaseous products based on the nitrogen content. For nitromethane this yields :

Deficiency in gaseous products (c.c. at *N.T.P.*).

| | Represented as C, H, and O. | | | Represented as $CH_2O$ and $H_2O$. | |
|---|---|---|---|---|---|
| | C. | O. | H. | $CH_2O$. | $H_2O$. |
| Expt. I ................ | 32·7 | 60·3 | 121·8 | 32·7 | 27·6 |
| Expt. II ................ | 32·3 | 57·1 | 114·9 | 32·3 | 24·8 |

It will be seen that the amounts of hydrogen and oxygen are nearly equivalent. Hence the deficiency in each case may be represented in terms of water and a carbohydrate, monomeric formaldehyde being chosen for the purpose of tabulation. On this basis the full analysis of the products from nitromethane can be tabulated as follows in terms of c.c. at *N.T.P.*

| | $CH_3{\cdot}NO_2$ decomp. | $N_2$. | CO. | NO. | $CO_2$. | $CH_2O$. | $H_2O$. | Residue. |
|---|---|---|---|---|---|---|---|---|
| Expt. I ........... | 40·6 | 14·9 | 5·7 | 10·8 | 2·2 | 32·7 | 27·6 | 2·2 |
| Expt. II ........... | 38·3 | 13·5 | 2·8 | 11·3 | 2·2 | 32·3 | 24·8 | 2·2 |

In view of these results and of the simplicity of the nitromethane molecule itself, it was immediately apparent that formaldehyde might be a primary product. Accordingly, further experiments were performed to test for its presence among the products of irradiation. This was readily confirmed : after the vapour had been irradiated for 5 hours, the liquid gave a strong positive reaction for formaldehyde both with Nessler's and with Schryver's solution. In addition, globules of an immiscible liquid were floating in the nitromethane. These were readily identified as water by f. p. and also by means of anhydrous copper sulphate, which rapidly absorbed them and immediately turned blue.

For nitroethane, assuming as before that the gaseous nitrogen compounds give a true measure of the amount of decomposition, we calculate the deficiency of carbon, hydrogen, and oxygen in the gas phase at the temperature of − 80°. This deficiency, in agreement with the results with nitromethane, is fairly closely expressible in terms of acetaldehyde and water, thus :

Deficiencies (c.c. at *N.T.P.*).

| | Obs. | 21 c.c. $H_2O$ + 12·6 c.c. $CH_3{\cdot}CHO$ require | Diff. |
|---|---|---|---|
| C ................ | 25·6 | 25·2 | + 0·4 |
| H .............. | 90·1 | 92·4 | − 2·3 |
| O ................ | 35·5 | 33·6 | + 1·9 |

A further experiment was now carried out in which the liquid was refluxed in the quartz tube as before, while the vapour was irradiated with the mercury lamp for 12 hours. The liquid residue was then examined : it was found to be mainly unchanged nitroethane, but on its surface were a few small globules of a colourless liquid which was identified as water as before. The presence of acetaldehyde was confirmed in the liquid residue by the following series of colour reactions and controls, the latter being designed to expose any possible interference by the nitrogen dioxide which was known to be present.

A very dilute solution of acetaldehyde was made up and a few crystals of sodium nitrite added to it (solution A); also a dilute solution of sodium nitrite was prepared (solution C); the specimen is designed by B.

(1) An alkaline solution of sodium nitroprusside gave a deep red colour with A and B, and no colour with C.

(2) Nessler's solution gave a brown precipitate rapidly turning grey with A and B, and no reaction with C.

(3) Benzidine hydrochloride gave a yellow coloration which faded in 30 minutes with A and B, and no colour with C in very dilute solution. A strong solution of C gave a brown colour, probably by a diazo-reaction.

(4) 2 : 4-Dinitrophenylhydrazine in hydrochloric acid gave a lemon-yellow colour, rapidly turning orange, with flocculation, with A and B, and produced a white precipitate with C.

These experiments confirm the presence of water and acetaldehyde and eliminate the effect of nitrogen dioxide; also (1) serves to distinguish the aldehyde from formaldehyde, which gives no coloration with sodium nitroprusside.

The full analysis can now be tabulated as follows (c.c. at *N.T.P.*) :

| $C_2H_5\cdot NO_2$ decomp. | $N_2$. | CO. | $\underbrace{\text{NO.}\quad NO_2.}$ | $CO_2$. | $C_2H_4$. | $CH_3\cdot CHO$. | $H_2O$. | Residue. |
|---|---|---|---|---|---|---|---|---|
| 25·7 | 9·1 | 4·8 | 7·5 | 1·8 | 9·6 | 12·6 | 21 | 2·6 |

The results of the analysis, although at first sight complicated, thus lead unmistakably to the conclusion that formaldehyde and acetaldehyde are products in the photodecomposition of nitromethane and nitroethane respectively. It will now be shown that, if it be further assumed that these aldehydes are primary products in the decomposition, the rest of the analytical data can be readily interpreted in terms of the secondary reactions which must follow. We shall therefore conclude that primary reactions of the following type occur :

$$CH_3\cdot NO_2 \longrightarrow CH_2O + NOH \qquad (1)$$

$$C_2H_5\cdot NO_2 \longrightarrow CH_3\cdot CHO + NOH \qquad (2)$$

It is remarkable that this primary change is in close analogy with that established by Anderson, Crumpler, and Hammick for the photochemical decomposition of nitroso*iso*propylacetone and β-nitroso-βε-dimethylhexane, *viz.*,

$$h\nu + Me_2C(NO)\cdot CH_2R = \tfrac{1}{2}H_2N_2O_2 + CMe_2{:}CHR$$

As in their case, the other products of reaction can be accounted for as decomposition and oxidation products of the free oximino-radical NOH; *e.g.*, writing

$$2\,NOH = H_2O + N_2 + O \qquad (3)$$

followed, in the case of nitromethane, by

$$O + CH_3\cdot NO_2 = CH_2O + HNO_2 \qquad (4)$$

$$2HNO_2 = H_2O + NO + NO_2 \qquad (5)$$

$$NO_2 + CH_2O = NO + H_2O + CO \qquad (6)$$

we obtain, on applying appropriate factors and combining the equations with equation (1) :

|  | $6CH_3\cdot NO_2 =$ | $5CH_2O +$ | $2N_2 +$ | $2NO +$ | $4H_2O +$ | CO |
|---|---|---|---|---|---|---|
| Expt. I .............. | 6·0 | 4·8 | 2·15 | 1·6 | 4·0 | 0·83 (1·2) |
| Expt. II .............. | 6·0 | 5·0 | 2·15 | 1·8 | 3·95 | 0·45 (0·95) |

Below the equation are given the experimental figures reduced to a basis of 6 vols. of nitromethane decomposed. There is obviously good agreement. Two values are shown under CO in each case, those in parentheses having been obtained by adding in the volume of carbon dioxide found in the experimental results. In view of the deficiency of nitric oxide and excess of nitrogen it seems probable that some oxidation of carbon monoxide to dioxide occurred. It is clear, however, that the results can be satisfactorily accounted for in terms of the primary mechanism of equation (1), followed by simple oxidation reactions.

The products from nitroethane can be accounted for in terms of alternative oxidation reactions. Thus, if reactions (2) and (3) are followed, *e.g.*, by reactions

$$C_2H_5\cdot NO_2 + O = C_2H_4 + HNO_3 \qquad (7)$$

$$2HNO_3 = H_2O + 2NO_2 + O \qquad (8)$$

$$HNO_3 + C_2H_5\cdot NO_2 = 2CO + 3H_2O + N_2 \qquad (9)$$

$$CO + NO_2 = CO_2 + NO \qquad (10)$$

then, by application of appropriate factors to (2), (3), (7), (8), (9), and (10) and adding, we obtain the stoicheiometric equation

| $16C_2H_5\cdot NO_2 =$ | $8CH_3\cdot CHO +$ | $6N_2 +$ | $6C_2H_4 +$ | $12H_2O +$ | $3CO +$ | $CO_2 +$ | $\underbrace{3NO_2 + NO}$ |
|---|---|---|---|---|---|---|---|
| 16·0 | 8·0 | 5·7 | 6·0 | 12·4 | 3·1 | 1·1 | 4·8 |

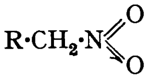
The experimental figures reduced to the basis of 16 vols. of nitroethane are shown below the equation and are in good agreement.

## DISCUSSION.

The apparently complicated analytical results therefore point unmistakably in both cases to identical primary reactions, and these are the more interesting since they have been shown to apply to nitroso-compounds as well.

This must be regarded as an important clue to the nature of the primary act. Our knowledge of the mechanism is limited, but the fact that in the nitroso-compounds studied by Anderson, Crumpler, and Hammick it is not possible for the nitroso-group to take up any isomeric form, suggests that with the nitro-compounds reaction must also be identified with some form of the molecule which possesses a true nitroso-group. Thus, of the two isomeric modifications (I) and (II), we conclude that it is the form (I) whose light absorption is responsible for the reaction.

(I.)

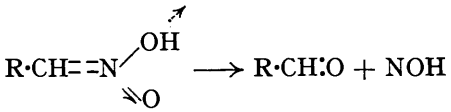


$$R{\cdot}CH_2{\cdot}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

(II.)

$$R{\cdot}CH{:}N\begin{smallmatrix}\nearrow OH\\ \searrow O\end{smallmatrix}$$

This is not to say that reaction does not take place through some structure analogous to (II). Since an oximino-group is actually split off, it is clear that a hydrogen atom must come into close association with the nitroso-group at some stage of the change, and the simplest way in which this can be visualised is to suppose that light absorption throws the molecule into the form (II) and that the following change occurs :



$$R{\cdot}CH{=}{=}N\begin{smallmatrix}\nearrow OH\\ \searrow O\end{smallmatrix} \longrightarrow R{\cdot}CH{:}O + NOH$$

A rough estimate of energy required for this change can be computed from Sidgwick and Bowen's estimated values of the heats of formation of the C=C and the C=N link, and by assuming that the heat of formation of N⇌O is half that of N=O, the value of which was calculated by Anderson, Crumpler, and Hammick as 114·3. In this way we find that an absorption of energy of *ca.* 43 cals. is required, though this value must be regarded as only very approximate in view of the fact that the bond energies are not yet fixed with certainty and, in particular, are subject to a correction for the $^5S \rightarrow {}^3P$ transition in the carbon atom, as already pointed out by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103). The calculation, however, is sufficient to show that a light quantum of 90 cals. or more, which is what we are concerned with in the present case, is fully adequate to provide the required energy.

The tautomeric change envisaged above as preceding the final rupture of the molecule is analogous to, though not identical with, the mechanism suggested by Anderson, Crumpler, and Hammick for the nitroso-compounds, as can be seen by comparing the two cases.

Nitroso-compounds. Nitro-compounds.

We may therefore assume that both arise from the same cause, *viz.*, the close approach of a hydrogen atom to the electronically excited nitroso-group at some stage in the vibration of the molecule after light absorption.

## SUMMARY.

The nature of the primary photochemical change in the photochemical decomposition of the vapours of nitromethane and nitroethane has been examined. Light absorption, mainly continuous, occurs beyond 3000 A., and it is shown that the products of decomposition can be represented quantitatively as resulting from a primary change $h\nu + R{\cdot}CH_2{\cdot}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} = R{\cdot}CHO + NOH$, followed by secondary reactions of decomposition and oxidation by the oximino-radicals.

The relationship of this change to an analogous one discovered in nitroso-compounds by Anderson, Crumpler, and Hammick is discussed.

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