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PHOTOCHEMISTRY OF NITROALKANES*

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INTRODUCTION

The behaviour of nitroalkanes in the presence of electromagnetic radiation has been a subject of interest for over forty years. The yellowing of these compounds in sealed tubes under the influence of light was first noted in Plotnikow's monograph *Allgemeine Photochemie*[1]. The ready decomposition of nitroalkanes, both photochemically and thermolytically, facilitates study. The number of papers relating to the photochemistry of nitroalkanes has therefore increased considerably over the last 10 years. Advances in instrumentation now enable a thorough analysis of the nitroalkane decomposition products, as well as examination of the primary processes occurring under the action of electromagnetic radiation.

It should be mentioned here that reasonably refined studies in the field of radiation chemistry of nitroalkanes, and in particular on the radiolysis of these compounds, were begun a few years ago[2–11]. The studies were aimed both at identifying the products from the action of ionizing radiation on nitroalkanes and also determining the mechanism of their formation.

In investigations of the photochemistry of nitroalkanes particular attention must be paid to photofragmentation. Nitroalkanes have been photolyzed in gas, liquid, and solid (frozen matrices) states. The dissociation energy for simple nitroalkanes is about 60 kcal mol^{-1}. Bonds with a similar dissociation energy can easily be broken by light with a wavelength greater than $\lambda = 360$ nm. Most studies, however, have been done with polychromatic ultra-violet light, or at the specific wavelengths of 313 nm and 253.7 nm. The ultra-violet absorption spectra of liquid nitroalkanes in typical solvents (alcohols, cyclohexane, water) lie in the range 270–280 nm (see Fig. 1), and are practically solvent independent[12,13].

The infra-red spectra for nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane indicate the presence of the characteristic NO_2 group—the symmetrical stretching vibrations (1361 cm^{-1}) and the asymmetrical stretching vibrations (1558 cm^{-1})[14]; overtones of these bands[15] have also been assigned.

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* A paper dedicated to Professor R.G.W. Norrish, FRS.

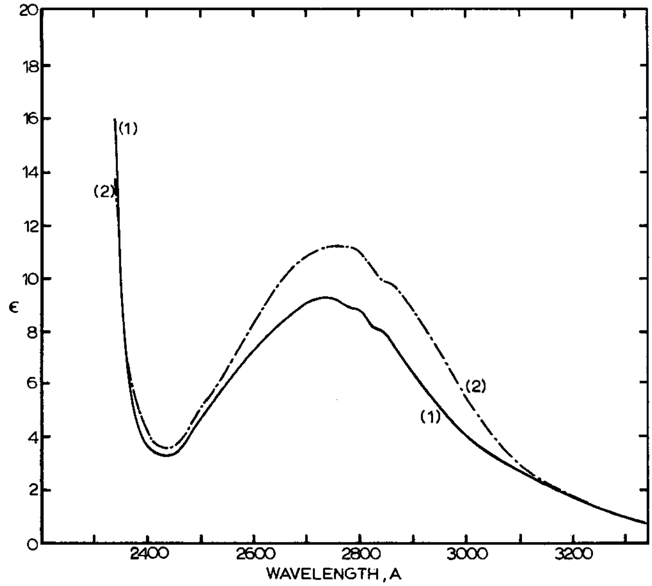


Fig. 1. Absorption spectra of (1) nitromethane, CH_3NO_2 (g) at 25° C and (2) nitroethane, $C_2H_5NO_2$ (g) at 25° C. [From J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, Wiley, New York, 1967.]

One of the first photochemical studies on nitroalkanes was carried out by Norrish and Hirschlaff[16]. The nitromethane was irradiated at 101° C with ultra-violet light and a number of the photolytic products, such as N_2, NO, CO, H_2O and CH_2O, were identified. Later, several other workers dealt with the photolysis of nitroalkanes using both static and dynamic methods. The identified products and the phases employed for irradiation are reported in Table 1.

The analytical techniques include qualitative classical analysis, spot analyses, ultra-violet and infra-red spectroscopy, gas–liquid chromatography, and mass spectrometry. Rebbert and Slagg[17] determined quantum yields for certain photolysis products of nitromethane and nitroethane as well as their rates of formation. The quantum yields for formation of these products are small (of the order of 10^{-1}–10^{-3}) and were found to be increased when shorter wavelength light was used. Nicholson[18] (gas phase) and Paszyc[2,3] (liquid phase) have determined quantitatively the photodecomposition products of these nitroalkanes and report the fractional amounts of the photolysis products formed. The findings indicate that the conversion is insignificant and amounts to about 2 percent. Chachaty and coworkers[19,20] endeavoured to identify the free radicals produced in certain nitroalkanes irradiated both in the liquid phase and frozen in matrices in the presence of polar compounds like tetrahydrofuran (THF) or simple alcohols using electron paramagnetic resonance (e.p.r.) spectroscopy. Recently Reid and Tucker[21] investigated the photoreaction of nitroethane with cyclohexane and with diethyl ether. The scavenging role of nitromethane in an aqueous acetone–nitro-

TABLE 1

PHOTOLYSIS PRODUCTS OF SOME SIMPLE NITROALKANES

Nitroalkane	Phase	Source of light	Photolysis products	Refs.
CH_3NO_2	gas, liquid	full spectrum of u.v. light light pressure lamp 313 nm, 253,7 nm	H_2, CO, CO_2, N_2(?), NO, NO_2, CH_4, C_2H_6 CH_3ONO, CH_3O, NO_2, CH_3, OH, HCOH, CH_3NO lower poly(oxymethylene glycols), paraformaldehyde	2, 3, 16–18, 44
$C_2H_5NO_2$	gas, liquid	as above	H_2, CO, CO_2, N_2(?), NO, NO_2, H_2O, CH_4, C_2H_4, C_2H_6, C_3H_8, CH_3CHO, C_2H_5ONO, para-aldehyde	2, 3, 17
$(CH_3)_2CHNO_2$	gas, liquid	full spectrum of u.v.	NO_2, C_3H_6, H_2O, CH_3COCH_3, $(CH_3)_2ONO$, $(CH_3)_2CHOH$, CH_3CN	35

ethane system was also investigated[22]. The results of these studies will be discussed later.

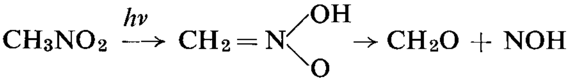
PRIMARY PROCESSES IN THE PHOTOCHEMICAL DECOMPOSITION OF NITROALKANES

Nitromethane

One of the first attempts to elucidate the primary mechanism was that reported by Norrish and Hirschlaff[16]. The authors photolyzed nitromethane vapour and on the basis of the observed stoichiometry:

$$6\,CH_3NO_2 \rightarrow 5\,CH_2O + 2\,N_2 + 2\,NO + 4\,H_2O + n\,CO \qquad (1)$$

suggested that light absorption resulted in isomerization followed by molecular elimination of formaldehyde and nitroxyl:



$$CH_3NO_2 \xrightarrow{h\nu} CH_2{=}N\langle{}^{OH}_{O} \rightarrow CH_2O + NOH \qquad (2)$$

This mechanism is in agreement with the observation of Dalby[23] who identified the NOH radical in the gas phase flash photolysis of nitromethane. It is significant that Hillenbrand and Kilpatrick[24] in their studies on the pyrolysis of this compound in a flow system found that the molar yield of formaldehyde, extrapolated to zero contact time, was unity. Similar conclusions were drawn by Christie *et al.*[25] who found that the products of photolysis included nitrosomethane and formaldehyde, the yield of the latter being unaffected by the addition of nitric oxide, which was held to be an indication that formation of formaldehyde was *via* a molecular elimination reaction.

Brown and Pimentel[26] have photolyzed nitromethane in a solid argon matrix at 77 K. They postulate the primary process to be an isomerization to *cis*-methyl nitrite. They suggest that the methyl nitrite is the unstable intermediate mentioned by Hirschlaff and Norrish. In later gas phase studies by Pimentel and Rollefson[27] and by Rebbert and Slagg[17], methyl nitrite was also found and its formation was explained by the following reactions:

$$CH_3NO_2 \xrightarrow{h\nu} CH_3 + NO_2 \qquad (3)$$

$$CH_3 + NO_2 \rightarrow CH_3ONO \qquad (4)$$

In the gas phase, since there is excess energy, most of the nitrite decomposes to CH_3O and NO, whereas in the solid phase a rapid deactivation stabilizes the methyl nitrite (compare Napier and Norrish[28]). These workers have shown, using the flash photolysis method, that nitromethane decays to yield methyl radicals and nitrogen dioxide, and that the fragments thus formed may subsequently recombine to give CH_3ONO, or disproportionate to yield methoxyl and nitric oxide:

$$CH_3NO_2 \xrightarrow{h\nu} CH_3 + NO_2 \tag{3}$$

$$CH_3 + NO_2 \rightarrow CH_3ONO \tag{4}$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO \tag{5}$$

McGarvey and McGrath[29] also observed the spectrum of the methyl radical at short intervals after flash photolyzing nitromethane.

The primary mechanism[3] is further corroborated by the results of the studies by Bielski and Timmons[30], who demonstrated the presence of the methyl radical and of nitrogen dioxide in the e.p.r. spectra of nitromethane photolyzed at 77 K (Figs. 2 and 3). In the spectrum of Fig. 2, a, b and c refer to the main triplet of lines and d, e and f to the other triplet. According to the Bielski and Timmons the average separation of the a–b–c triplet lines is 58 G. This agrees well with the reported value of 57.8 G[31]. The corresponding value for the d–e–f triplet is 46 G, which is also in good agreement with the value of 45 G estimated from the work of Jen *et al.*[31]. In addition to these six lines in the e.p.r. spectrum there is only a quartet of lines, as indicated in Fig. 2. The total separation of these four lines is 65 G. This is in close agreement with values reported in the literature for the methyl free radical[31,32].

The occurrence of reaction (3) was thought to be responsible for the comparatively significant methane yields obtained by Rebbert and Slagg[17] and by Nicholson[18] in the gas phase and by Paszyc[2,3] in the liquid phase. It was proposed that the other major products (see Table 1), carbon monoxide, nitric oxide, nitrogen dioxide, hydrogen and ethane arose from the following reactions:

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{6}$$

$$CH_2NO_2 + M \rightarrow CH_2O + NO + M \tag{7}$$

$$NO_2 \rightarrow NO + O \tag{8}$$

$$O + CH_3 \rightarrow CO, CO_2, CH_3OH, CH_2O \tag{9}$$

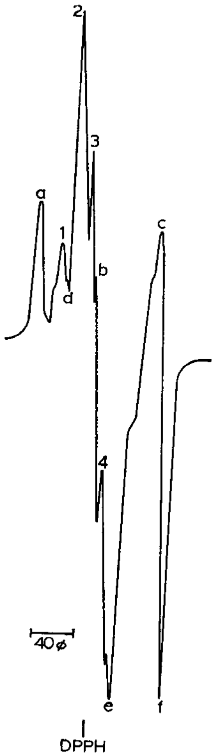
$$2\,CH_3 \rightarrow C_2H_6 \tag{10}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \tag{11}$$

Napier and Norrish[28] in their studies on the flash photolysis of nitromethane identified several of the fragments from their absorption spectra (Table 2 and Fig. 4). Their results furnished substantial evidence for the primary mechanism of photolysis.

The essential results of these studies can be summarized as follows:

(1) Flash photolysis of nitromethane under isothermal conditions results in the formation of methyl radicals with a high concentration at the shortest delay. These radicals are subsequently rapidly removed from the system.



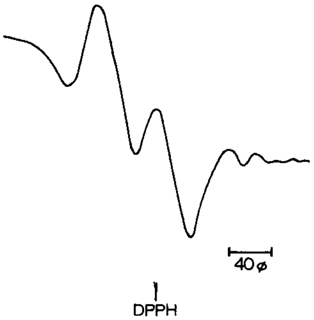


Fig. 2. E.p.r. spectrum of nitrogen dioxide and the methyl radical produced during the photolysis of nitromethane at 77 K. [From B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, 68 (1964) 347.]

Fig. 3. E.p.r. spectrum of nitrogen dioxide at 77 K. This spectrum was obtained after annealing the photolyzed nitromethane sample shown in Fig. 2 at −80° C. [From B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, 68 (1964) 347.]

(2) Under non-isothermal conditions the spectra of the OH radical and of nitrogen dioxide appear at the shortest delay. At later delays, weak spectra of the nitrosomethane monomer and dimer are observed, as are the spectra of formaldehyde and methyl nitrite.

(3) The addition of nitric oxide to a mixture of nitromethane and nitrogen results in enhancement of the nitrogen dioxide spectrum at the shortest delay after the flash, and the appearance of a strong spectrum of monomeric nitrosomethane (Fig. 4).

The results of these studies were compared with the findings from the flash photolysis of nitromethane under adiabatic conditions. Such radicals as NH, CN, and also nitroxyl were identified under these conditions.

Recently Norrish presented a new approach for elucidating some problems in photolysis of nitromethane partly based on the results of Napier and Norrish[28].

TABLE 2

THE FLASH PHOTOLYSIS OF NITROMETHANE

Spectra observed	Time of appearance after the flash	Time to reach max. intensity	Remarks
	Flashing CH_3NO_2 (0.03 mm) plus 3000-fold excess of N_2:		
CH_3	No delay	No delay	Decays within 34 μs
NOγ (0,0) and (1,0)	No delay	Indefinable	—
	Flashing CH_3NO_2 (0.8 mm) plus 400-fold excess of N_2:		
NOγ (0,0)	No delay	51 to 76 μs	—
OH (0,0)	No delay	No delay	Decays within 34 μs
	Flashing CH_3NO_2 (13 mm) plus 30-fold excess of N_2:		
OH (0,0) and (1,1)	No delay	No delay	Decays within 64 μs
CH_2O	322 μs	41 ms	0.5 mm formed
NO_2	No delay	No delay	0.1 mm formed; no increase apparent at longer delays
CH_3ONO	46 ms	—	0.5 mm formed with a 3330 J flash
CH_3NO	—	—	observed weakly a 1 min delay but not at 169 μs or 30 min
$(CH_3NO)_2$	—	—	observed weakly at 30 min delay

These results, taken together with earlier studies of continuous photolysis, help to construct a fairly consistent picture of the reaction mechanism. There can be little doubt in view of the immediate appearance of methyl radicals and nitrogen peroxide that the primary reaction is expressed by reaction (3).

This is in agreement with the conclusion of Pimentel and Rollefson[27] who observed the production of methyl nitrite in the gas phase, which they explained by reaction (3) followed by reaction (4). The observation of Napier and Norrish that, in the presence of nitric oxide, methyl nitrite is completely replaced by nitrosomethane is accounted for by the suppression of reaction (4) by the powerful scavenging reaction:

$$\dot{C}H_3 + NO \rightarrow CH_3NO \tag{12}$$

This complete suppression of reaction (4) also accounts for the great increase of NO_2 in the initial products when NO is present.

Since NO_2 is produced simultaneously with the flash, it will be subject to secondary photolysis:

$$NO_2 + h\nu \rightarrow NO + O \tag{13}$$

and this production of oxygen atoms in the initial stage of the reaction will account

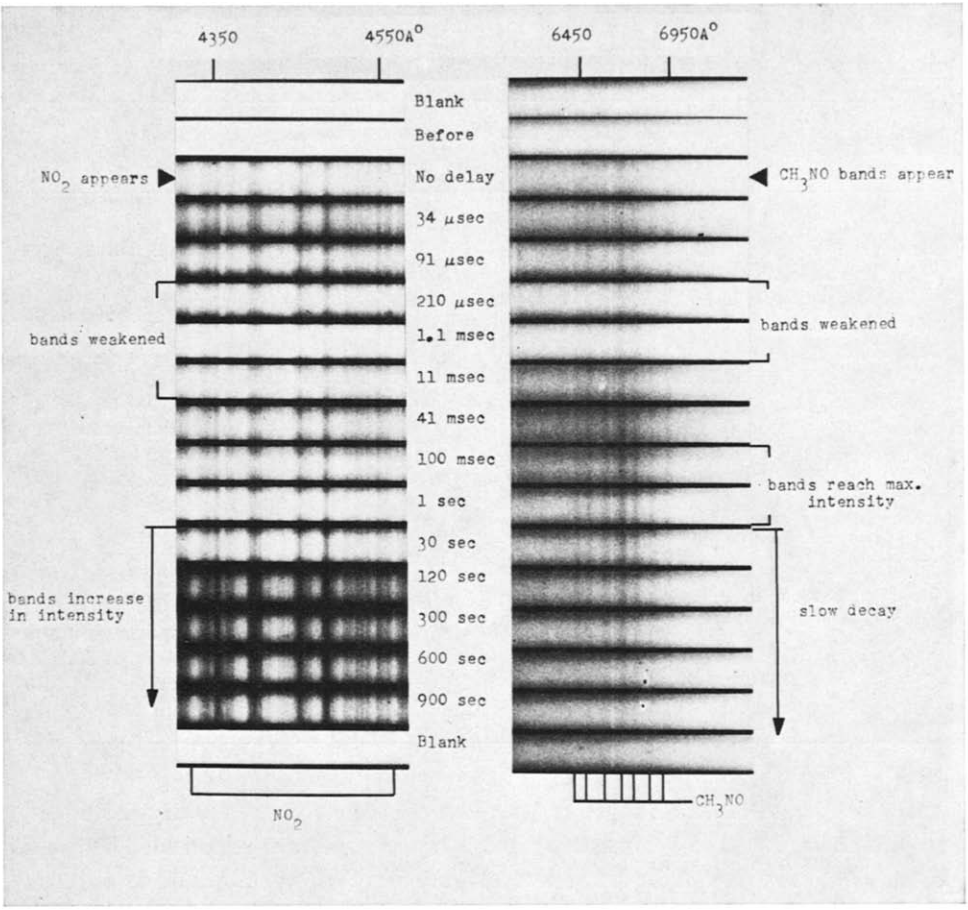


Fig. 4. The formation of nitrosomethane and nitrogen dioxide from the flash photolysis of: CH_3NO_2 (13 mm) + NO (20 mm) + N_2 (360 mm). [From J. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc. (A)*, 299 (1967) 317.]

for the concomitant appearance of the weak spectrum of hydroxyl as a result of hydrogen abstraction from nitromethane:

$$O + CH_3NO_2 \rightarrow OH + CH_2NO_2 \tag{14}$$

while the subsequent decomposition of the CH_2NO_2 radical would yield formaldehyde and nitric oxide:

$$CH_2NO_2 \rightarrow CH_2O + NO \tag{15}$$

which is not influenced by the presence of NO. If this reaction were the only source of formaldehyde it would account for the observation of Christie *et al.*[25], that the yield of formaldehyde, obtained by the continuous photolysis of nitromethane, is independent of the presence of nitric oxide. An alternative source of the CH_2NO_2 radical is, however, hydrogen abstraction by methyl radicals:

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{16}$$

though the formaldehyde derived from this source would clearly be suppressed by the presence of nitric oxide. This reaction can account for the production of methane observed by Nicholson[18] and would explain why in flash photolysis the spectrum of formaldehyde is only observed in the absence of nitric oxide. The results of Christie *et al.* may be explained if the nitrogen dioxide accumulating in their static system under continuous photolysis converted the reaction to a predominantly photocatalyzed decomposition of nitromethane by NO_2 *via* reactions (15), (16) and (17) followed by the disproportionation of NO:

$$4\ NO \rightarrow 2\ NO_2 + N_2 \tag{17}$$

This latter reaction has been proved to occur readily in the presence of nitrosomethane by Christie *et al.*[25] and by Phillips and Shaw[33].

The simultaneous decrease in intensity of CH_3NO and NO_2 after flashing can be explained by the reaction:

$$CH_3NO + NO_2 \rightarrow CH_3NO_2 + NO \tag{18}$$

which was shown to be almost complete by Phillips and Shaw[33] at 100°C, a plausible temperature for near isothermal flash conditions. The regrowth of the spectra of nitrosomethane and NO_2 at long delays is, however, less clearly explicable.

There remains the possibility of an additional primary reaction for the photolysis of nitromethane involving a molecular elimination reaction (2) such as that proposed by Hirschlaff and Norrish in 1936[16] which is in part supported by the detection of NOH by Dalby[23] in flash photolysis, and by Christie *et al.*[23]. In view of all the evidence now available there can be little doubt that the major part of the reaction proceeds by a free radical mechanism such as that which has been given above. Experimental work on the photocatalytic role of NO_2 in nitromethane decomposition is in progress.

In conclusion, it should be pointed out that the results of photolytic studies on nitromethane substantiate the suggestion of those authors[2,3,17,18,28,34] who believe that the primary process in the photochemical decomposition of nitromethane is reaction (3) although an additional primary photoreaction (1) cannot be completely ruled out.

Nitroethane

The studies on photolysis of nitroethane in the gas or liquid phases or in solid matrices have not been as extensive and detailed as for nitromethane. The problem has been dealt with by several authors, particularly by Rebbert and

Slagg, and by Paszyc, who discuss the primary mechanism of photolysis of this compound. The photolysis products of nitroethane are listed in Table 1.

The nature of the primary mechanism is not certain.

Rebbert and Slagg[17] suggest the following two primary steps for photolysis of this compound both in the liquid and solid phases:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 \tag{19}$$

$$C_2H_5NO_2 \rightarrow C_2H_4 + HONO \tag{20}$$

These authors found ethylene among the photolysis products of nitroethane and found that the quantum yield for the formation of ethylene is not conversion dependent and is not reduced by the addition of oxygen. The intramolecular rearrangement probably occurs through a four- or five-membered ring.

The author of this present paper believes that ethylene can be formed in the secondary disproportionation reaction of ethyl radicals, which occurs parallel to the recombination process:

$$2\ C_2H_5 \rightarrow C_4H_{10} \tag{21}$$

$$2\ C_2H_5 \rightarrow C_2H_4 + C_2H_6 \tag{22}$$

rather than through reaction (20). Attempts were made to find n-butane among the products of the nitroethane photolysis reaction. The primary mechanism of photodecomposition of nitroethane in reaction (19) is also advanced by Bielski and Timmons[30], who reportedly identified NO_2 and, presumably, also the C_2H_5 radical, upon irradiating nitroethane in a matrix at 77 K.

The formation of ethyl nitrite, acetaldehyde and ethane (and according to Paszyc, also ethylene and propane) as the products of nitroethane photolysis provide further evidence for reaction (19):

$$\nearrow C_2H_5 + NO_2 \tag{23}$$

$$C_2H_5 + NO_2 \longrightarrow C_2H_5ONO \tag{24}$$

$$\searrow C_2H_5O^* + NO \tag{25}$$

$$C_2H_5O^* + NO \rightarrow C_2H_5ONO \tag{26}$$

$$CH_3CHO + HNO \tag{27}$$

$$\nearrow C_2H_5 + CH_3CHO \tag{28}$$

$$C_2H_5 + C_2H_5O$$

$$\searrow C_2H_5OC_2H_5 \tag{29}$$

$$2\ C_2H_5 \rightarrow C_2H_4 + C_2H_6 \tag{22}$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \tag{30}$$

The presence of methyl nitrite and methane in the products of the nitroethane photolysis can be explained in terms of reaction (25) in which the excited ethoxy radical is formed and then decomposed:

$$C_2H_5O^* \rightarrow CH_3 + CH_2O \tag{31}$$

The methyl radical can then react as described for nitromethane[4-6,12,13]. The value of the activation energy of reaction (31) amounts to 12 ± 2 kcal mol^{-1} [17].

However, in reaction (25) there is an excess of 20 kcal mol^{-1} which is more than enough for reaction (31) to proceed isothermally. The other alternative to explain the formation of methyl radicals is C–C bond cleavage as a primary process. This seems very unlikely since at $\lambda = 313$ nm there is barely enough energy for such a process.

The results of the studies on photolysis of nitroethane indicate that the reactions of this compound occur largely following the primary process (19) and not (22), although the latter cannot be completely excluded.

1-Nitropropane, 2-nitropropane and tetranitromethane

Relatively little attention has been paid to the photolysis of these three compounds. Bielski and Timmons[30] investigated the photolysis of 1-nitropropane and of tetranitromethane at low temperature using polychromatic light from a high-pressure mercury lamp as in their experiments with nitromethane. They followed the formation of free radicals by the e.p.r. method (Fig. 5). For 1-nitropropane they observed formation of NO_2 as well as the C_3H_7 radical. However, their interpretation of the spectrum of the C_3H_7 radical is very involved and ambiguous, the situation being complicated by the number of protons in the radical.

Fig. 5. E.p.r. spectrum of photolyzed tetranitromethane at 77 K. [From B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, 68 (1964) 347.]

The electron paramagnetic resonance spectra studied furnish evidence for the following course of the photolysis for tetranitromethane:

$$C(NO_2)_4 + h\nu \rightarrow C(NO_2)_3 + NO_2 \tag{32}$$

The photolysis of 2-nitropropane both in the gas and liquid phases is being studied by the present author[35]. The gas phase photolysis of this compound was carried out at 130°C (a temperature at which this compound is thermolytically stable) in a glass flow system with a quartz reaction chamber.

The compound was photolyzed for varying time intervals, ranging from ~ 30 min to 10 h using not only a full spectrum of ultra-violet light, but also monochromatic light of wavelength 253.7 nm and 366 nm. The reaction products were identified by spectrophotometric methods and by gas–liquid chromatography (see Table 1). It is noted that, for a fixed wavelength and exposure time, identical products were isolated from both liquid and vapour phase irradiations. However, the *yield* of any one compound was phase dependent. For example, at 366 nm, vapour phase irradiation yields principally acetone and acetonitrile (along with nitrogen dioxide), whereas in the liquid phase reaction they appear in only trace amounts.

From the identified reaction products the primary mechanism of the photolysis of 2-nitropropane can be tentatively suggested to be:

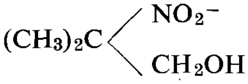
$$(CH_2)_3\,CHNO_2 + h\nu \begin{array}{ll} \nearrow (CH_3)_2CH + NO_2 & (33) \\ \searrow CH_3CH{=}CH_2 + HNO_2 & (34) \end{array}$$

Another part of the investigations—the photochemical properties of nitroalkanes—consist of the studies of the French authors[19,20] previously cited. These workers were concerned with the photolysis of nitrocompounds, including nitroalkanes, in the wavelength range 230–350 nm in solvents that are good proton donors such as water, tetrahydrofuran and simple alcohols. Free radicals formed from the photolysis reaction at room temperature in the liquid phase were discovered using the e.p.r. method. In particular, the very water-soluble 2-nitro-2-methylpropanol was studied. The photolysis was carried out both in neutral and in alkaline ($KOH = 10^{-2}$–$1\ N$) aqueous solutions.

After prolonged photolysis of a solution of this compound in triply distilled water a weak e.p.r. spectrum was observed, part of which was an unassignable multiplet, the balance being ascribed to the following radical:

$$[(CH_3)_2C\text{–}CH_2OH]_2\,N\text{–}\dot{O}\ (a_N = 16.1\ G) \tag{35}$$

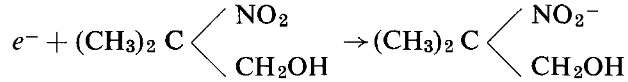
Photolysis of a solution in the pH range 12–14 gave a species, the e.p.r. spectrum of which showed a triplet with hyperfine structure, and coupling constant $a_N =$ 26 G. This was assigned to the radical anion:



$$(CH_3)_2C\begin{cases} NO_2^{-} \\ CH_2OH \end{cases} \tag{36}$$

The mechanism of formation of the radical is as follows:

$$OH^- \xrightarrow{h\nu} OH^\cdot + e^- \qquad (37)$$

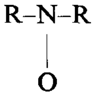


$$e^- + (CH_3)_2C(NO_2)(CH_2OH) \rightarrow (CH_3)_2C(NO_2^-)(CH_2OH) \qquad (38)$$

Irradiation of nitroalkanes of the RNO_2 type in solvents of the general formula R′H leads to the formation of the following four types of free radicals:

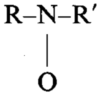
$R\dot{N}O_2H$

(I)



$R{-}\dot{N}(O){-}R$

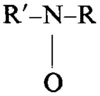
(II)



$R{-}\dot{N}(O){-}R'$

(III)

and



$R'{-}\dot{N}(O){-}R$

(IV)

The proposed mechanism for the formation of these photolysis products was substantiated by studies using deuterated compounds. The formation of radicals (II) and (III) may be explained by the following mechanism:

$$RNO_2 \xrightarrow{h\nu} (RNO_2)^* \qquad (39)$$

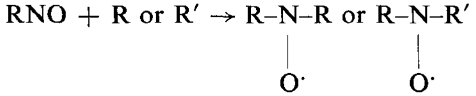
$$(RNO_2)^* \rightarrow R^\cdot + NO_2 \qquad (40)$$

$$(RNO_2)^* + R'H \rightarrow R\dot{N}O_2H + R' \qquad (41)$$

$$R + R'H \rightarrow RH + \dot{R} \qquad (42)$$

$$2\,R\dot{N}O_2H \rightarrow RNO_2 + RNO + H_2O \qquad (43)$$

$$2\,RNO \rightleftarrows (RNO)_2 \qquad (44)$$



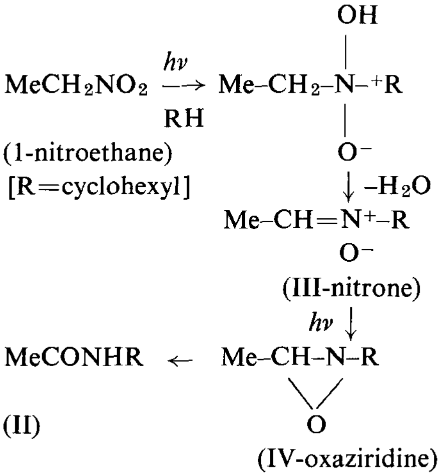
$$RNO + R \text{ or } R' \rightarrow R{-}N(O^\cdot){-}R \text{ or } R{-}N(O^\cdot){-}R' \qquad (45)$$

The formation of these radicals leads to the observed diamagnetic product. When the irradiated mixture of nitromethane in ethanol was evaporated it gave the dimer $(CH_3NO)_2$ as indicated by its characteristic ultra-violet spectrum (maximum at $\lambda = 266$ nm).

Nitroalkanes, as mentioned before, mainly provide three types of free radicals—(II), (III) and (IV). The value of the C–N bond energy in nitroalkanes is in the region of 2.5 eV[36], whereas the energy of the light absorbed in the studies by Chachaty and coworkers was higher than 4 eV. Hence there is more than sufficient energy to cause the C–N bond to break to yield free radicals energetic enough to abstract hydrogen from the solvent.

The bond energy for the bonds $CH_3...H$, $(CH_3)_2C...H$, $(CH_3)_2(CH_2OH)C...H$, are 104, 94.5, and 90 kcal mol^{-1} [37], respectively, whereas the bonding energy of hydrogen in the OH group of the alcohol amounts to 90 kcal mol^{-1}. Methyl and CH_3–CH–CH_3 radicals disappear completely as the result of hydrogen abstraction from the solvent (reaction 42) without furnishing a radical of the R–N–R type. The French authors in their papers give a summary of the free radicals formed as the result of irradiation of nitroalkanes in polar solvents along with the e.p.r. hyperfine splitting constants. These differ significantly.

Reid and Tucker[21] irradiated a solution of nitroethane in cyclohexane and in diethyl ether, using a Hanovia medium-pressure mercury arc (450 W) surrounded by a water-cooled quartz thimble. Acetamidocyclohexane (II) and 1-acetoamido-1-ethoxyethane, isolated from the irradiated mixtures, are the results of initial hydrogen abstraction by the excited nitro-group:


(1-nitroethane)
[R=cyclohexyl]
(III-nitrone)
(II)
(IV-oxaziridine)

1-Acetamido-1-ethoxyethane was also obtained by irradiation of 2-nitropropane in diethyl ether, presumably by loss of a methyl group during photorearrangement of the dimethyloxaziridine. Recently the continuous photolysis at λ=253.7 nm of acetone in aqueous solution in the presence of nitromethane was reported by Tran-Dinh-Son and Sutton[22]. They proved that methyl radicals produced from the photolysis of aqueous acetone are efficiently scavenged by nitromethane. From the resulting decrease in the methane and ethane yields at 22° C a value of 140 ± 15 was deduced for the rate constant ratio, k_7/k_4, of the reactions:

$$CH_3 + CH_3COCH_3 \xrightarrow{k_7} CH_4 + CH_2COCH_3$$

and $$CH_3 + CH_3NO_2 \xrightarrow{k_4} CH_3NO_2CH_3$$

It should be emphasized that the formation of the reaction products and their yields in the photolysis of nitroalkanes can be affected by atomic oxygen produced from the photochemical decomposition of nitrogen dioxide according to the following primary process:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (46)$$

At $\lambda = 366$ nm and at $\lambda = 313$ nm photodissociation is virtually complete. Sato and Cvetanovic[38] found that in the wavelength range 253.7–228.8 nm the primary process in nitrogen dioxide photolysis is the following:

$$NO_2 + h\nu \rightarrow NO + O(^1D) \qquad (47)$$

The above two mechanisms do not exhaustively cover this problem and more detailed data on the primary photolysis processes of NO_2 and on the secondary reactions can be found in refs. 39–42.

To sum up the results of the studies on the primary photolysis processes of nitroalkanes, it should be said that the first step is the dissociation of the C–N bond *i.e.*

$$RNO_2 \rightarrow R + NO_2 \qquad (48)$$

The mechanism fits moderately well for nitromethane. However, from Norrish's latest results[43] on photolysis of nitromethane in the gas phase (at different pressures, temperatures and wavelengths) the primary reactions:

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO + O \qquad (49)$$

$$CH_3NO_2 + h\nu \rightarrow CH_3NO + O \qquad (50)$$

cannot be excluded. The process (50) was suggested earlier by Cundall[8] for liquid nitromethane photolysis. For more complex nitroalkanes additional primary processes should be taken into consideration, specifically reaction (20) for nitroethane and (34) for 2-nitropropane. Confirmation or otherwise of mechanisms (20) and (34) could rest on accurate data from flash photolysis, kinetic spectroscopy and e.p.r. spectroscopy.

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