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PHOTOLYSIS OF NITROSOCOMPOUNDS. Part II[1]. ESTER EXCHANGE REACTIONS IN THE PHOTOLYSIS OF GEM CHLORONITROSOCOMPOUNDS.

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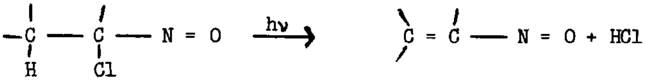
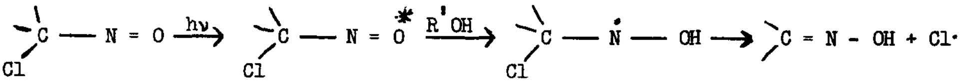
Recent communications[2,3,4] on the photochemistry of geminal chloronitrosocompounds prompt us to report some of our results which have implications for the mechanisms proposed in this field of study. It is apparent from these recent reports that the earlier dehydrochlorination mechanism proposed by Mitchell and Cameron[5] is incorrect.

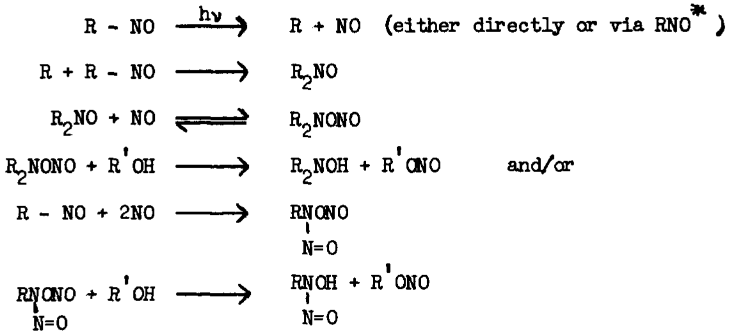


The results obtained by de Boer *et al.*[3] and by Duynstee and Mevis[4] strongly suggest that the initial photochemical decomposition of geminal chloronitrosocompounds always takes place by C-N fission. C-Cl fission, proposed by Creagh and Trachtenberg[2] to account for the different product distribution observed on photolysis of methanol solutions of 2-chloro-2-nitrosobutane compared with benzene solutions, is inadmissable on energetic grounds [D(C-NO)[6] = 34-41 kcal.mole^{-1}. D(C-Cl)[7] = 76-80 kcal.mole^{-1}.] The energy of the incident light employed is 45 kcal.mole^{-1}. The alternative reaction



scheme is ruled out by the absence of the required formaldehyde[2,3,4](R=Me) or acetone[4] (R=Pr^{iso}). It is therefore apparent that the fate of the solvent is important for all photolysis mechanisms in hydrogen donating solvents.

We have observed that an important product in the photolysis of gem chloronitrosocompounds in alcohols (R$'$OH) is the corresponding nitrite (R$'$ONO). It appears that this product has been overlooked by other workers due to the experimental techniques employed. In the case of methanol the corresponding nitrite is gaseous and thus unless precautions are taken to trap the methyl nitrite, the product will escape. In addition to this the nitrites may themselves be photolysed unless the irradiating wavelengths employed specifically exclude the appropriate wavelength range. When these precautions are taken it is possible spectrophotometrically to monitor the nitrite formed throughout photolysis of an alcoholic solution of a geminal chloronitrosocompound and to relate this to the consumption of the nitrosocompound itself. Our studies on fifteen nitrosocompounds in methanol and isopropanol indicate that this is a general reaction and reference to the Table shows two examples where for every mole of nitrosocompound decomposed between 0·3 and 0·5 moles of nitrite are formed. We suggest that an ester exchange reaction, well known for the production of lower alkyl nitrites[8] is of importance. A basic reaction scheme will involve the following



$$R - NO \xrightarrow{h\nu} R + NO \quad \text{(either directly or via } RNO^{*}\text{)} \qquad (1)$$

$$R + R - NO \longrightarrow R_2NO \qquad (2)$$

$$R_2NO + NO \rightleftharpoons R_2NONO \qquad (3)$$

$$R_2NONO + R'OH \longrightarrow R_2NOH + R'ONO \quad \text{and/or} \qquad (4)$$

$$R - NO + 2NO \longrightarrow R\underset{\substack{|\\ N=O}}{N}ONO \qquad (5)$$

$$R\underset{\substack{|\\ N=O}}{N}ONO + R'OH \longrightarrow R\underset{\substack{|\\ N=O}}{N}OH + R'ONO \qquad (6)$$

The equilibrium (3) will normally lie well over to the left hand side but the rapid irreversible reaction (4) will cause equilibrium (3) to move completely to the right hand side. Ginsburg[9] has noted the occurrence of reaction (6) when $R = CF_3$ and $R' = CH_3$.

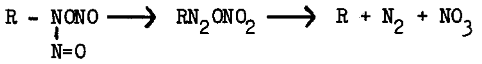
Product distribution will depend upon the subsequent reactions of the hydroxylamine derivatives from (4) and (6). In the absence of hydroxylic solvents other reaction patterns are possible e.g. in benzene the N-nitrosohydroxylaminenitrite

Compound	Time for complete photolysis (min.)	Initial RNO concentration (10^{-3} moles/lit)	Pr^{iso} ONO concentration (10^{-3}moles/lit)	$\frac{Pr^{iso}\ ONO\ found}{RNO\ consumed}$
A	9	11·42	4·78	0·42
A	14	22·84	9·08	0·40
A	21	49·7	17·83	0·36
A	40	79·6	27·07	0·34
A	90	99·4	28·66	0·29
B	6	5·58	2·14	0·38
B	9	9·78	3·98	0·41
B	15	13·97	6·52	0·47
B	18	22·3	9·70	0·44

A = 3-chloro-3-nitrosopentane

B = trichloronitrosomethane.

can rearrange to the diazonium nitrate with subsequent production of nitrogen.



$$R - \underset{\displaystyle N{=}O}{N}ONO \longrightarrow RN_2ONO_2 \longrightarrow R + N_2 + NO_3 \qquad (7)$$

The fact that nitrogen is only a minor product[4] for the photolysis of these compounds in alcohols is thus readily explicable. In the absence of alcohol, equilibrium (3) will play only a minor role and reactions (4) and (6) will of course be absent.

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REFERENCES

1 Part I. J.R. Dickson and B.G. Gowenlock, *Annalen*, **745**, 152 (1971).

2 L. Creagh and I. Trachtenberg, *J. Org. Chem.*, **34**, 1307 (1969).

3 A.H.M. Kayen, L.R. Subramanan and Th.J. de Boer, *Rec. Trav. Chim.*, **90**, 866 (1971).

4 E.F.J. Duynstee and (Miss) M.E.A.H. Mevis, *Rec. Trav. Chim.* **90**, 932 (1971)

5 S. Mitchell and J. Cameron, *J. Chem. Soc.*, 1964 (1938).

6 P.J. Carmichael, B.G. Gowenlock and C.A.F. Johnson, *Int. J. Chem. Kinetics*, (in the press)

7 J.A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

8 G. Bertoni, *Gazz. Chim. Ital.*, **12**, 438 (1882).

9 V.A. Ginsburg, L.L. Martinova and M.N. Vasil'eva, *Zhur. Obshch. Khim.*, **37**, 1083 (1967).