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PHOTOLYSIS OF 1-NITROPROPANE IN GAS PHASE

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Primary processes in photolysis of 1-nitropropane in gas phase are analogous to those of nitroethane and 2-nitropropane. Ethylene, propylene and methyl nitrite are the major photolysis products, while minor products are methane, methyl nitrate, ethylene oxide, ethyl nitrite, propyl nitrite, formaldehyde, propionaldehyde, water, nitric oxide and nitrogen dioxide. Quantum yields of formation of photoproducts ethylene and propylene at 22°C are 0.074 and 0.042; and at 56°C these are 0.039 and 0.01. A mechanism of the photolysis is suggested.

The photochemistry of simple nitroalkanes have continued to attract considerable attention and has recently been reviewed.[2] Primary nitroalkanes undergo photochemical reactions involving homolytic cleavage of C-N bond in gas phase[3] and an intermolecular hydrogen abstraction process from the solvent, in solution phase.[4-6] Although the primary process for the photolysis of nitromethane is[7]:

$$RNO_2 + h\nu \longrightarrow R^{\bullet} + NO_2^{\bullet}$$

another process suggested by Cundall et al.[8]:

$$CH_3NO_2 + h\nu \longrightarrow CH_3NO^{\bullet} + O$$

and by Norrish[9]:

$$CH_3NO_2 + h\nu \longrightarrow CH_3^{\bullet} + NO + O$$

cannot be ruled out.

For more complex nitroalkanes like nitroethane, 1-nitropropane and 2-nitropropane, additional primary processes have to be considered. Although the nature of the primary processes of nitroethane photolysis is not certain, Rebbert and Slagg[10] suggested the following two primary steps for photolysis of nitroethane:

$$C_2H_5NO_2 + h\nu \longrightarrow C_2H_5^{\bullet} + NO_2^{\bullet}$$

$$C_2H_5NO_2 + h\nu \longrightarrow C_2H_4 + HONO$$

Bieleski and Timmons[11] obtained nitrogen dioxide during the photolysis of 1-nitropropane and suggested C-N bond scission and the formation of NO_2 in the photolysis of complex aliphatic nitro compounds. However, Paszyc[12] suggested the following primary mechanism of photolysis of 2-nitropropane:

$$(CH_3)_2CHNO_2 + h\nu \longrightarrow (CH_3)_2CH^{\bullet} + NO_2^{\bullet}$$
$$\longrightarrow CH_3CH{=}CH_2 + HNO_2$$

Photolysis of 1-nitropropane is studied in gas phase and a mechanism of photolysis is suggested here. 1-Nitropropane obtained from Ralph N. Emanual, England (B.P. 132°C) was purified by trap to trap distillation until gas chromatographically pure and stored in the dark in a vacuum system at liquid nitrogen temperature. Photolysis was carried out in a cylinderical quartz vessel having optically flat windows. It was attached to the vacuum system using greaseless taps. A vacuum better than 10^{-4} torr was obtained by means of a mercury diffusion pump backed by a rotary oil pump. Reactant pressures in the photolysis vessel were measured with a manometer. Using a Hanovia medium pressure mercury arc (500 W) controlled by a voltage stabiliser, 1-nitropropane at a pressure of 7.5 mm Hg was irradiated for periods of between 1 minute and 4 hours. Product analysis after irradiation was achieved by gas chromatography employing a flame-ionization detector (for hydrocarbons) and a thermal conductivity detector (for other gases such as H_2, N_2, NO and NO_2), and by mass spectrometry. A specially designed stainless steel greaseless valve, employing silicone "O" ring seals, was used for sample injection. The quantum yield measurements are based on the assumption that $\Phi_{C_2H_4}=0.074$ is the quantum yield[10] of formation of ethylene during the photolysis of nitroethane for 3 minutes at 22°C.

Interestingly enough, the quantum yields of formation of ethylene and propylene during the photolysis of 1-nitropropane at room temperature (22°C) for 1 minute are 0.074 and 0.042; and at 56°C for 10 minutes photolysis, they are 0.039 and 0.01.

The major photolysis products of 1-nitropropane are found to be ethylene, propylene and methyl nitrite, while the minor products are methane, methyl nitrate, ethylene oxide, ethyl nitrite, propyl nitrite, formaldehyde, propionaldehyde, water, nitric oxide and nitrogen dioxide.

From the identified reaction products, the primary mechanism of the photolysis of 1-nitropropane can be suggested to be analogous to that of nitroethane[10] and 2-nitropropane[12]:

(A) $CH_3CH_2CH_2NO_2 + h\nu \longrightarrow CH_3CH{=}CH_2 + HONO$

(B) $CH_3CH_2CH_2NO_2 + h\nu \longrightarrow CH_3CH_2CH_2^{\bullet} + NO_2^{\bullet}$

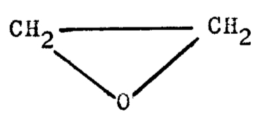
Formation of ethylene is due to the reaction:

1. $CH_3CH_2CH_2^{\bullet} \longrightarrow CH_3^{\bullet} + CH_2{=}CH_2$ [13]

and methyl nitrite is formed by the reaction:

2. $CH_3^{\bullet} + NO_2 \longrightarrow CH_3ONO$ [14]

For formation of methyl nitrate, methane, ethyl nitrite, ethylene oxide, propyl nitrite, formaldehyde, propionaldehyde, water, nitric oxide and nitrogen dioxide, the following reaction mechanism is suggested:

3. $CH_3^{\bullet} + CH_3CH_2CH_2NO_2 \longrightarrow CH_4 + CH_2CH_2CH_2NO^{\bullet}$
4. $CH_3^{\bullet} + NO_2 \longrightarrow CH_3O^{\bullet} + NO$
5. $CH_3^{\bullet} + CH_3O^{\bullet} \longrightarrow CH_4 + HCHO$
6. $CH_3O^{\bullet} + NO_2 \longrightarrow CH_3ONO_2$
7. $CH_3O^{\bullet} + NO \longrightarrow CH_3ONO$
8. $Pr^{\bullet} + NO_2 \longrightarrow PrONO$
9. $Pr^{\bullet} + NO_2 \longrightarrow PrO + NO$
10. $Pr^{\bullet} + NO_2 \longrightarrow CH_3CH{=}CH_2 + HONO$
11. $2\ HONO \longrightarrow H_2O + NO + NO_2$
12. $PrO + NO \longrightarrow CH_3CH_2CHO + HNO$
13. $PrO + NO_2 \longrightarrow CH_3CH_2CHO + HONO$
14. $PrO \longrightarrow C_2H_5^{\bullet} + HCHO$
15. $C_2H_5^{\bullet} + NO_2 \longrightarrow C_2H_5ONO$
16. $CH_2CH_2CH_2NO_2^{\bullet} \longrightarrow$  $+ NO + HCHO$

The apparatus, experimental techniques and other details would be the subject of a forthcoming publication.

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