

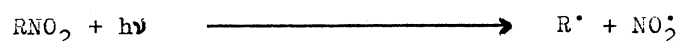
# PHOTOLYSIS OF 1-NITROPROPANE IN GAS PHASE

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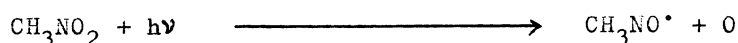
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Primary processes in photolysis of 1-nitropropane in gas phase are analogous to those of nitroethane and 2-nitropropane. Ethylene, propylene and methyl nitrite are the major photolysis products, while minor products are methane, methyl nitrate, ethylene 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.

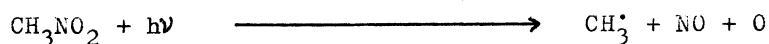
The photochemistry of simple nitroalkanes have continued to attract considerable attention and has recently been reviewed.<sup>2</sup> Primary nitroalkanes undergo photochemical reactions involving homolytic cleavage of C-N bond in gas phase<sup>3</sup> and an intermolecular hydrogen abstraction process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



another process suggested by Cundall et al.<sup>8</sup>:

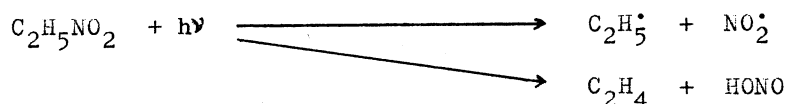


and by Norrish<sup>9</sup>:



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<sup>10</sup> suggested the following two primary steps for photolysis of nitroethane:



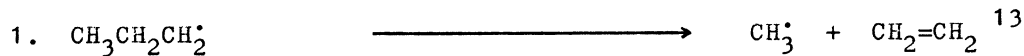
$$\begin{array}{lcl} (\text{CH}_3)_2\text{CHNO}_2 + h\nu & \xrightarrow{\hspace{1cm}} & (\text{CH}_3)_2\dot{\text{C}}\text{H} + \text{NO}_2^\bullet \\ & \searrow & \text{CH}_3\text{CH=CH}_2 + \text{HNO}_2 \end{array}$$

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.

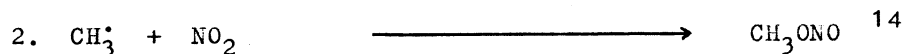
From the identified reaction products, the primary mechanism of the photolysis of 1-nitropropane can be suggested to be analogous to that of nitroethane<sup>10</sup> and 2-nitropropane<sup>12</sup>:



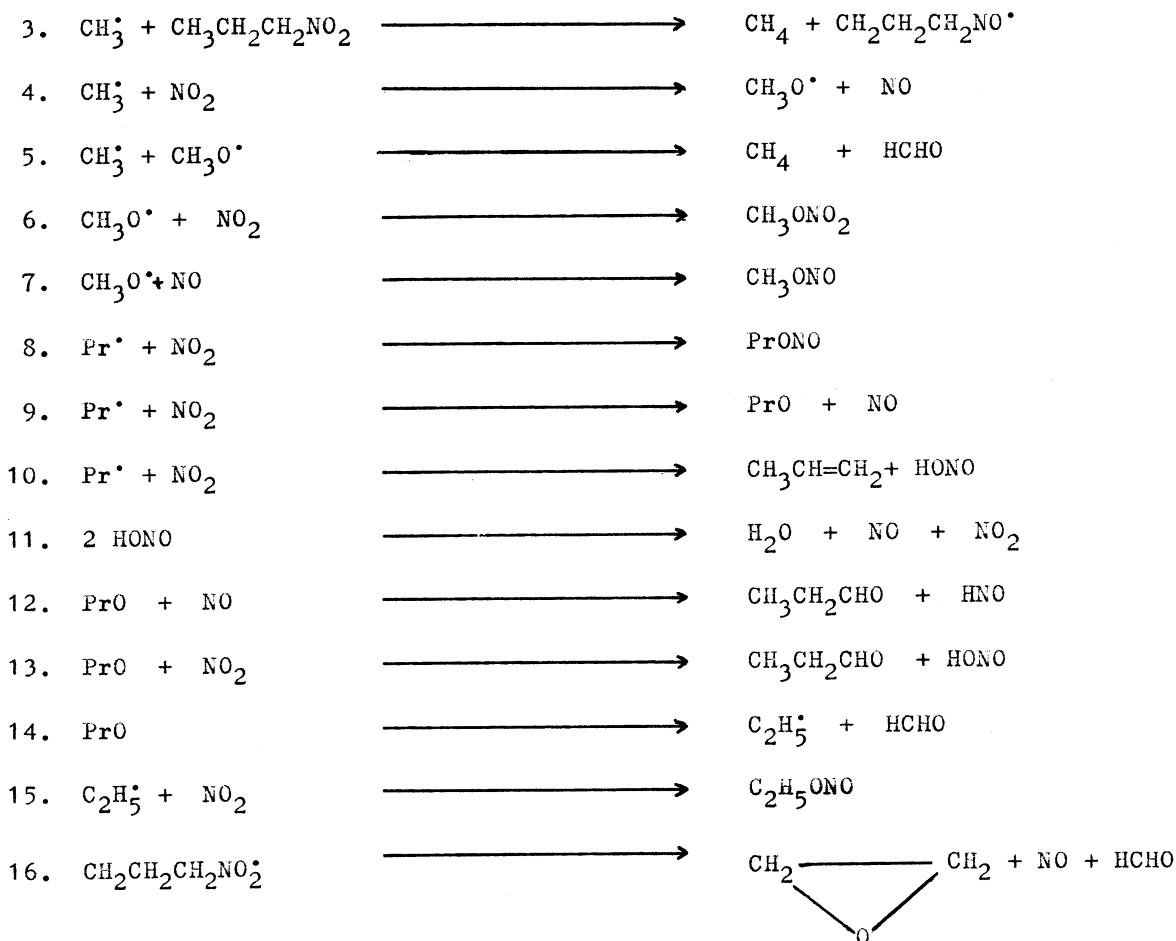
Formation of ethylene is due to the reaction:



and methyl nitrite is formed by the reaction:



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:



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

## REFERENCES:

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(Received May 28, 1975)