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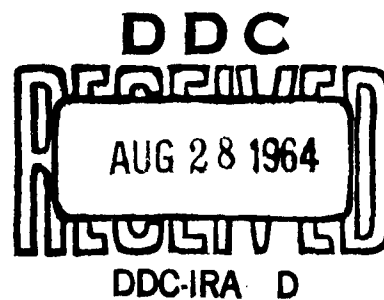
AZOXYCOMPOUNDS

I. THE PHOTOLYSIS OF AZOXYMETHANE

B. G. Gowenlock

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ABSTRACT

A study of the photolysis of azoxymethane has been made. The reaction products include nitrogen, nitrous oxide, methane, and ethane. The ratio $N_2:N_2O$ is independent of temperature and two primary photolytic processes are postulated to account for this fact. On the assumption that methane arises from the reaction $CH_3 + CH_3N_2OCH_3 \rightarrow CH_4 + CH_2N_2OCH_3$, the activation energy of this reaction is 6 ± 2 kcal/mole. Other reactions that take place during the photolysis are discussed.

INTRODUCTION

Azoxymethane and other azoxyalkanes were prepared by Langley, Lythgoe, and Rayner in 1952 (1). A survey of the literature indicates that little attention has been directed to these compounds, the bulk of the published work relating to aromatic azoxyalkanes. By analogy with azoalkanes, it is expected that the primary photolytic (2) and pyrolytic (3) processes will produce two radicals and nitrous oxide. Thus for azoxymethane we expect the reaction [1] to occur.

[1]
$$CH_3-N=N-CH_3 \xrightarrow{h\nu} CH_3 + N_2O + CH_3.$$
$$\downarrow$$
$$O$$
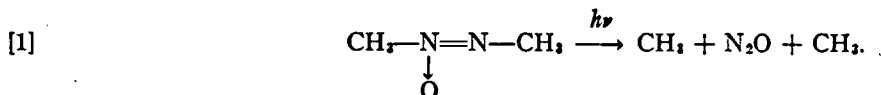
EXPERIMENTAL

Materials

Azoxymethane was prepared by Dr. L. C. Leitch and Mr. N. Kraut by the literature method (1). It was a colorless, mobile liquid with a vapor pressure of about 20 mm at 20 °C. A sample was vaporized and its ultraviolet spectrum determined with a Cary recording spectrophotometer. This spectrum was similar to that given for an ethanol solution (1) and the wavelength of maximum absorption was 212–213 mμ (217 mμ in ethanol (1)). Reference samples of other materials for mass spectrometry and gas chromatography were provided by Dr. F. P. Lossing.

Apparatus

A conventional photolysis apparatus was used. The light source was a Hanovia S-500 medium pressure mercury arc operated on a regulated supply. It was used without filter or lens in order to allow sufficient products to be accumulated in a run of one hour's duration. The beam of light from the lamp passed through two copper tubes, which connected the lamp to the reaction vessel (5 cm diameter and 15 cm length). A piece of thick cardboard could be inserted between the two tubes in order to shut off the arc from the reaction vessel. The reaction vessel could be heated electrically and was mounted in a hot box. The reaction system was isolated from the reactant reservoir gas analysis apparatus and main vacuum line by greaseless mercury cut-offs. Pressures of reactants were measured by means of a spiral gauge, mounted within the hot box, and used as a null instrument in conjunction with a mercury U-tube manometer.

Procedure and Analysis

Thoroughly degassed azoxymethane was admitted to the reaction vessel and the pressure measured. The light beam was allowed to enter the reaction vessel and the run allowed to proceed for 1 h. The products of the run were trapped out at liquid nitrogen temperatures and the remaining noncondensable gases transferred to a combined Toepler/gas burette. After the quantity of the gas was measured, the sample was transferred to a mass spectrometer sampling tube. On occasion a portion was also transferred to a

crusher tube for gas chromatographic analysis using a zeolite column. Further fractions were taken into the Toepler/gas burette, measured, and analyzed. The temperatures and analytical techniques employed were: $-160°$ (mass spectrometry), $-131°$, $-78°$, and room temperature (gas–liquid chromatography). All gas–liquid chromatographic analyses were carried out on a Perkin–Elmer fractometer, using a 1 m column of Carbowax 1500 on powdered teflon, helium carrier gas, 50 °C, flow rate 150 cc/min.

RESULTS AND DISCUSSION

The most volatile reaction products were nitrogen, nitrous oxide, methane, and ethane. It was shown by both mass spectrometry and gas chromatography that hydrogen, oxygen, and nitric oxide were absent from the reaction products. The azoxymethane concentration was not varied significantly; the temperature was varied from 27° to 121°, and the ratio $N_2:N_2O$ remained constant at 0.20 ± 0.02 (8 runs). This constancy suggests that the nitrogen is produced by a primary process and the simplest reaction that can be written to account for this is:

[2]
$$CH_3-\overset{\underset{\displaystyle \downarrow}{}}{\underset{\displaystyle O}{N}}=N-CH_3 \xrightarrow{h\nu} CH_3 + N_2 + OCH_3.$$
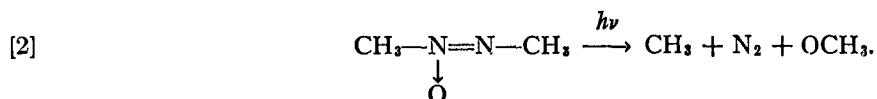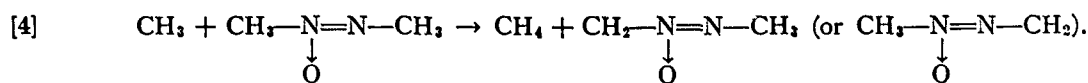
Reaction [2] is presumed to take place simultaneously with reaction [1]. Further support for the occurrence of nitrogen elimination from azoxymethane is given by pyrolyzing azoxymethane on a heated quartz surface ($\simeq 600$ °C) in the inlet of a mass spectrometer, where the primary decomposition process [3] takes place,

[3]
$$CH_3-\overset{\underset{\displaystyle \downarrow}{}}{\underset{\displaystyle O}{N}}=N-CH_3 \rightarrow CH_3OCH_3 + N_2,$$
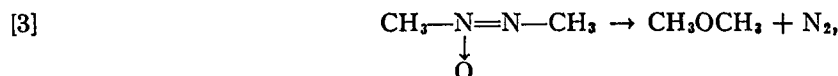
and any production of methyl radicals is consequent upon decomposition of the dimethyl ether. (The author is indebted to Dr. F. P. Lossing for this observation.) In addition, pyrolysis of a sample of azoxymethane at about 340 °C for 3.5 h produced nitrogen and nitrous oxide in the ratio 0.92, again indicating the importance of nitrogen production. These observations were contrary to our initial expectation and further investigation is underway. We are unaware of any evidence in the literature for thermal or photolytic production of nitrogen from azoxy compounds, and note that the reaction [2] is more favorable thermochemically than reaction [1] by about 50 kcal/mole (4).

Methane and ethane are prominent reaction products and it is likely that these will be produced from reactions [4] and [5] respectively.
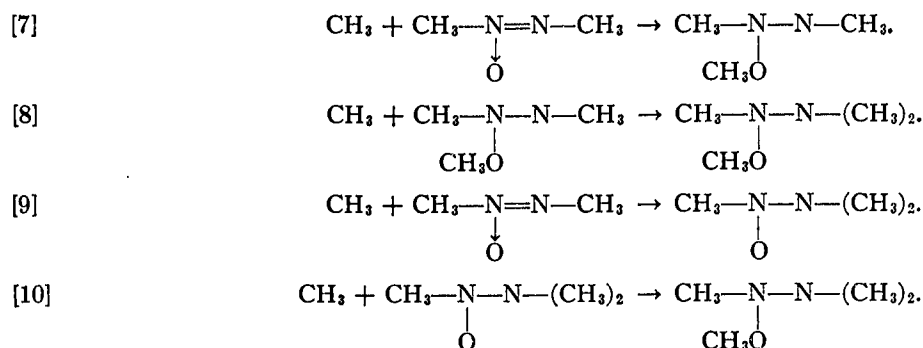
[4]
$$CH_3 + CH_3-\overset{\underset{\displaystyle \downarrow}{}}{\underset{\displaystyle O}{N}}=N-CH_3 \rightarrow CH_4 + CH_2-\overset{\underset{\displaystyle \downarrow}{}}{\underset{\displaystyle O}{N}}=N-CH_3 \ (or \ CH_3-\overset{\underset{\displaystyle \downarrow}{}}{\underset{\displaystyle O}{N}}=N-CH_2).$$

[5]
$$CH_3 + CH_3 \rightarrow C_2H_6.$$

Consequently, preliminary values have been obtained for the kinetic parameters of reaction [4], $E_4 = 6\pm2$ kcal/mole, $P_4 \simeq 10^{-2}$. It is to be emphasized that these are only preliminary values; it is hoped to obtain a greater number of points over a wider range of experimental conditions. These values compare favorably with those obtained (2) for the comparable reaction [6], $E_6 = 7.6\pm0.2$ kcal/mole, $P_6 \simeq 10^{-3}$.

[6]
$$CH_3 + CH_3N=NCH_3 \rightarrow CH_4 + CH_2N=NCH_3.$$

The ratio $(\frac{1}{2}CH_4 + C_2H_6)/N_2O$ was less than unity and decreased smoothly from about 0.74 at 27° to 0.39 at 121°. Admittedly, this approach to the product balance ignores the contribution of reaction [2], but it makes possible a comparison with the

azomethane results (2) where the corresponding ratio fell from 0.85 at room temperature to 0.28 at 128°. It was therefore expected that methyl radicals would add to azoxy-methane in similar fashion to the azomethane reactions, i.e., [7] and [8] and (or) [9] and [10].

[7]
$$CH_3 + CH_3\text{—}N\text{=}N\text{—}CH_3 \rightarrow CH_3\text{—}N\text{—}N\text{—}CH_3.$$
$$\qquad\qquad\quad\downarrow\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\quad O\qquad\qquad\qquad CH_3O$$

[8]
$$CH_3 + CH_3\text{—}N\text{—}N\text{—}CH_3 \rightarrow CH_3\text{—}N\text{—}N\text{—}(CH_3)_2.$$
$$\qquad\qquad\qquad |\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\quad CH_3O\qquad\qquad\qquad CH_3O$$

[9]
$$CH_3 + CH_3\text{—}N\text{=}N\text{—}CH_3 \rightarrow CH_3\text{—}N\text{—}N\text{—}(CH_3)_2.$$
$$\qquad\qquad\quad\downarrow\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\quad O\qquad\qquad\qquad\qquad O$$

[10]
$$CH_3 + CH_3\text{—}N\text{—}N\text{—}(CH_3)_2 \rightarrow CH_3\text{—}N\text{—}N\text{—}(CH_3)_2.$$
$$\qquad\qquad\qquad |\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\quad O\qquad\qquad\qquad\qquad CH_3O$$

Mass spectrometric investigations of the fractions resolved from g.l.c. analysis of the less volatile reaction products gave no peaks above 80 implying the absence of trimethyl methoxyhydrazine. It is possible that trimethylhydroxylamine (cracking pattern due to Bromberger and Phillips (5)) is formed, and also an azocompound $CH_3\text{—}N\text{=}N\text{—}OCH_3$. Discussion of routes to such products is postponed pending further more detailed investigation of the photolysis, and of reaction products from reaction of methyl radicals with azoxymethane. Methyl alcohol and trace quantities of dimethyl ether were identified from g.l.c. analysis.

A referee has suggested that nitrogen elimination could proceed by reaction [11],

[11]
$$CH_3\text{—}N\text{=}N\text{—}CH_3 \xrightarrow{h\nu} O + CH_3\text{—}N\text{=}N\text{—}CH_3,$$
$$\qquad\qquad\downarrow$$
$$\qquad\qquad O$$
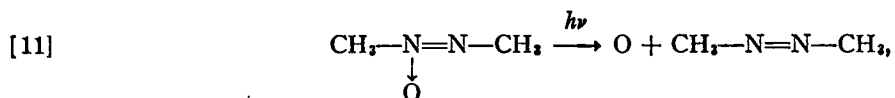
followed by photolysis of the azomethane to give nitrogen and hydrocarbon products. This possibility cannot be eliminated completely, but there is some evidence to suggest that it is unlikely. At least some tetramethylhydrazine would be expected as a reaction product, and the absence of peaks above 80 in the mass spectrum of the less volatile products is difficult to reconcile with the presence of azomethane implied by reaction [11]. Reaction [2] is more favorable than reaction [11] by about 70 kcal./mole. If reaction [11] does occur then the absence of oxygen and nitric oxide in the reaction products can be regarded as evidence for the absence of reactions [12] and [13] (because of unfavorable energy requirements, E_{12} and E_{13} being of the order 20 kcal/mole (6)),

[12] $O + N_2O \rightarrow 2NO$

[13] $O + N_2O \rightarrow N_2 + O_2,$

and the absence of oxygen atom recombination reactions. Photolysis of azoxymethane – nitric oxide mixtures and analysis for nitrogen dioxide reaction product may answer this problem, provided that there is no methyl radical catalyzed disproportionation of the nitric oxide under these reaction conditions. Further evidence against reaction [11] is to be found in the methyl alcohol reaction product of which the methoxy radical is the obvious precursor.

ACKNOWLEDGMENTS

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