PHOTOOXIDATION OF AZOMETHANE IV. THE ROLE OF FORMALDEHYDE¹

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ABSTRACT

The photooxidation of azomethane has been reinvestigated over a range of conversion extending to at least 7% at relatively high oxygen pressure and at 162° C. Kinetic and tracer (added $C^{13}H_2O$) studies support the view that the formaldehyde formed in the reaction can act as a source of the oxides of carbon. These were found to be enriched in C^{13} in the tracer work.

INTRODUCTION

One of the puzzling features of the mechanism of the photooxidation of azomethane (1) has been the nature of the product responsible for the self-inhibition (2, 3) of the reaction. Formaldehyde, nitrous oxide, and "excess nitrogen" (3) are produced at rates which decrease with the time of exposure. These products are thought (1, 3) to arise via the reactions

$$R + CH_3N_2CH_3 \rightarrow RH + CH_2 - N_2CH_3,$$
[1]

$$CH_{2}N_{2}CH_{2} + O_{2} \rightarrow N_{2}O + CH_{2}O + CH_{3}, \qquad [2]$$

$$\rightarrow N_2 + CH_2O + CH_3O, \qquad [3]$$

where R is some radical in the system and [2] and [3] are written as over-all processes which might occur in stages. Provided methyl and methoxyl, or radical products of their reaction with oxygen, can function as R in [1], the elements of a chain reaction are present in the mechanism as appears to be required by the data (3).

It was recognized (2, 3) that when this chain was inhibited by some product, the inhibition mechanism must involve the production of carbon monoxide and, probably, of carbon dioxide. The mechanism suggested was a competition for the radicals R by the inhibiting substance, here designated by R'H.

$$R + R'H \to RH + R'$$
^[4]

$R' + O_2 \rightarrow CO + other products$ [5]

$\rightarrow CO_2$ + other products [6]

It is postulated that the "other products" do not propagate chains to any extent. Initially it was suggested that formaldehyde should be identified as R'H (2). While this suggestion led to a satisfactory qualitative explanation of the phenomenon, it was not compatible with later (3) quantitative data. Therefore another mechanism, which identified R'H with performic acid, was advanced.

The purpose of the present work was to obtain data confirming, or otherwise, the hypothesis that formaldehyde could not function as R'H. In addition to a purely kinetic approach, experiments were done in which formaldehyde- C^{13} was added to the reaction system. From a kinetic point of view the concentration of formaldehyde found at the end of an experiment, including that formed in the reaction, is indicative of whether or not formaldehyde was consumed in the reaction. If such consumption did indeed

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occur, and if the mechanism of the consumption involves the inhibition mechanism [4], [5], and [6], the oxides of carbon found should be enriched in C^{13} .

EXPERIMENTAL

Apparatus

The vacuum apparatus, thermostatted air oven, and optical arrangements were essentially those used in an earlier investigation (3) with only minor modifications. The volume of the 5-cm diameter reaction cell was 180 cc, that of the complete reaction system, including the stirrer, 256 cc. All connecting tubing through which formaldehyde was required to pass could be heated to 140° C to prevent polymerization of that substance.

Materials

Azomethane (Merck of Canada, Montreal) was purified in the vacuum system in the usual manner (1, 2, 3). Gas chromatographic separation and estimation along with mass spectrometric identification of impurities revealed the presence in this sample of trimethyl hydrazine ($\langle 2\% \rangle$), methyl chloride ($\langle 0.1\% \rangle$), and methanol ($\langle 0.1\% \rangle$). The latter impurity was particularly objectionable in the experiments done at low conversions and, for these, it was removed by gas chromatography.

Oxygen was prepared by heating potassium permanganate and was separated from condensable impurities by passage through a trap at -196° C.

Formaldehyde-C¹³ (C¹³/C¹² = 20.4%) was obtained as required by heating a sample of enriched α -polyoxymethylene supplied by Dr. L. C. Leitch of these laboratories.

The trisodium salt of chromatropic acid (4,5-dihydroxy-2,7-naphthalene disulphonic acid, trisodium salt) used in the analysis of formaldehyde was prepared by titration of an aqueous solution (15%) of chromatropic acid disodium salt (Eastman Kodak) with a solution of sodium hydroxide (3%) to pH 7 as measured on a pH-meter. The salt was purified by fractional precipitation (3) and the beige-colored crystals were kept in dark bottles.

Procedure

Aside from minor details most operations in an experiment were done as described previously (3).

For the experiments with added formaldehyde- C^{13} , several break-seal bulbs, whose volumes were known, were filled from a manifold at one time using the filling technique developed earlier (3). The formaldehyde content of one bulb was determined and that of each of the others was calculated from the known volumes. Mixtures of azomethane, formaldehyde, and oxygen were prepared in the reaction system as described before (3).

Analysis of Products

After an exposure the products were condensed at -196° C in a U tube and the noncondensable gases (O₂, N₂, CO) were collected and analyzed over a hot mixture of copper and cupric oxide (1). Carbon dioxide and nitrous oxide were separated from a Le Roy still (4) at -160° C and analyzed by mass spectrometry. Small quantities of formaldehyde, methyl chloride (present as an impurity), and azomethane always appeared in this fraction and prevented accurate estimation of the major components. Some uncertainty is also introduced into the C¹³/C¹² ratio of the carbon dioxide because of the effects of these impurities.

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Formaldehyde was separated from the remaining liquid products by a single passage through a Le Roy still held at -130° C and condensed onto a frozen solution of the trisodium salt of chromatropic acid held at -196° C. All connecting tubing accessible to the formaldehyde vapor was held at 140° C. Procedures developed earlier (3) were followed in detail for the remaining steps in this modification of the chromatropic acid method (5). The liquid products were collected and analyzed for methanol by gas chromatography in a column developed by Blake and Kutschke (6) (25% dinonyl phthalate and 5% glycerol on Fischer Columpak; 29° C; H₂ flow rate, 45 cc/min). Peak areas were compared with those of standard samples.

RESULTS

Table I gives the data from several experiments at 162° C. The conditions were maintained as closely as possible to the earlier work (3). Oxygen concentration was sufficiently high to suppress completely the formation of methane and ethane. The trend of the

TABLE I
Yields of products in the photooxidation
$(p_{azo} = 57 \text{ mm}, p_{O_2} = 7 \text{ mm at } 0^\circ \text{ C}; \text{ reaction temperature, } 162^\circ \text{ C};$
$I_{\rm a}=4.0 imes10^{-13}{ m quanta/ccsec})$

	μmoles						
Time, minutes	N ₂	СО	CO2	N ₂ O	CH ₂ O	CH₃OH	
$1 \\ 2.5 \\ 4 \\ 5 \\ 15 \\ 15 \\ 25 \\ 35 \\ 45 \\ 55 \\ 20 \\ 40$	$\begin{array}{c}$	1.33 1.15 5.10 5.04 8.90 12.2 17.5 17.0 20.8 Oxygen	0.7 1.6 2.2 3.7 4.9 4.5 5.2 absent	$ \begin{array}{c}$	$ \begin{array}{c}$	$\begin{array}{c} \hline 0.8 \\ 1.4 \\ 2.2 \\ 4.0 \\ \hline 12.5 \\ 12.4 \\ 22.4 \\ 33.4 \\ 41.9 \\ 42.3 \\ 48.8 \\ \end{array}$	

yields with time is shown in Fig. 1 in which quantum yields of a product, defined as the ratio of the amount of a product formed per unit time to that of nitrogen formed in the absence of oxygen with otherwise identical conditions, are plotted as a function of conversion. The latter corresponds to D_1 of reference 2 and is calculated with the assumptions that (a) each molecule of azomethane which disappears gives rise to a molecule of nitrogen or of nitrous oxide, and that (b) the stirring was completely efficient. Aside from that of methanol and formaldehyde the general forms of the curves in Fig. 1 agree with those obtained earlier (2, 3).

Results from experiments with added formaldehyde-C¹³ are given in Table II. The amount of formaldehyde added corresponded to a concentration about twice as great as that found after long experiments without added formaldehyde. Figure 2 shows that the concentration of formaldehyde rapidly adjusts to that same, approximately steady,

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FIG. 1. Quantum yields as a function of conversion at 162° C: \bullet methanol, \bigcirc formaldehyde, \blacksquare nitrous oxide, \square secondary nitrogen, \blacktriangle carbon monoxide, \triangle carbon dioxide.

TABLE II

Yields of products in the photooxidation (Presence of 9.7 μ moles of formaldehyde-C¹³)

Time	μmoles			100C ¹³ /C ¹²	
minutes	N 2	СО	CH ₂ O	CO	CO_2
$ \begin{array}{c} 1 \\ 2 \\ 5 \\ 15 \\ 20 \\ \end{array} $	$ \begin{array}{r} \overline{} \\ 2.4 \\ 5.2 \\ 10.2 \\ 14.2 \end{array} $	$\begin{array}{c} 0.9 \\ 1.4 \\ 3.2 \\ 6.9 \\ 7.9 \end{array}$	$6.2 \\ 6.4 \\ 5.9 \\ 5.4 \\ 6.0$	$ \begin{array}{r} 12 \\ 16 \\ 13 \\ 12 \\ 13 \end{array} $	$ \begin{array}{r} 19\\ 14\\ 10\\ \hline 14\\ 14\\ \end{array} $

NOTE: Conditions as in Table 1.

concentration and thereafter remains unchanged. The yields of carbon monoxide obtained from experiments of low conversion were much greater in the presence of added formaldehyde than in its absence. This is shown in Fig. 3 as a plot of the absolute amounts of carbon monoxide formed at various times for the two sets of conditions. The slope of the curve (Fig. 3, open circles) obtained in the presence of formaldehyde becomes constant at about the degree of conversion at which the formaldehyde concentration reaches its approximately steady value (Fig. 2).

The last two columns of Table II present the data on the isotopic composition of the oxides of carbon found. There is little doubt that these compounds are enriched in C^{13} . Mixtures of formaldehyde- C^{13} and carbon monoxide were carried through the procedure of an experiment in the absence of ultraviolet illumination. On analysis no detectable enrichment was observed in the carbon monoxide.

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FIG. 2. Variation of the yield of formaldehyde with conversion: \bigcirc normal photooxidation, \bigcirc 9.8 µmoles formaldehyde-C¹³ added initially. FIG. 3. Variation of the yield of carbon monoxide with conversion: \bigcirc normal photooxidation, \bigcirc 9.8 µmoles formaldehyde-C¹³ added initially.

DISCUSSION

This report is concerned only with the reaction at 162° C with conditions used in earlier investigations (1, 2, 3) and is confined largely to the discussion of the likelihood that formaldehyde can inhibit the reaction under these conditions. Moreover, the discussion is limited to the region of conversion greater than about 1%. At lower conversions, reproducible data are very difficult to obtain.

In an earlier communication (3) several arguments were offered to refute the hypothesis that formaldehyde could participate in the inhibition mechanism. These were of two types: kinetic, which discussed the shape of the yield vs. time curves, and isotopic, which involved the results of a photooxidation experiment done in the presence of formaldehyde enriched in oxygen-18.

In considering the kinetic arguments it must be borne in mind that, to a precision of about 10-15%, good agreement between this and the earlier study is found in the

yield vs. time curves of many of the products. This agreement is excellent in the curves for total nitrogen, carbon monoxide, nitrous oxide and, with somewhat less precision, for secondary nitrogen and carbon dioxide. Analogous curves for formaldehyde and methanol yields differ significantly.

The present data indicate quite definitely that formaldehyde concentration does indeed approach a stationary value with time. The earlier data, covering a somewhat smaller range of conversion, did not exhibit such a limit although the existence of such a limit is not incompatible with those data. For some reason as yet unknown the limiting concentration, or possible limiting concentration in the case of the earlier work, found in the two sets of data differ by a factor of about two as does the time (or conversion) required to attain that limit. The excellent agreement between the yields of other products, especially those of carbon monoxide, indicate that the two sets of data were taken under very similar conditions. The only possible explanations involve either an unknown systematic error in one or the other analytical techniques (which were virtually identical) or a difference in surface characteristics causing this specific effect. At present no choice is possible between these alternatives.

More extensive data are presented here concerning the effect of added formaldehyde on the yields of some products. In particular, Fig. 2 shows that formaldehyde is not inert in the system as was required by the mechanism suggested earlier (3).

That the consumption of formaldehyde is accompanied by the production of carbon monoxide is indicated by the enhanced rate of production of that product when excess formaldehyde is present initially (Fig. 3). After formaldehyde has been depleted to approximately its stationary value (i.e. about 0.5% conversion, Fig. 2), the yield-time curve for the formation of carbon monoxide is not inconsistent with a rate of production similar to that found in the absence of added formaldehyde (Fig. 3).

The C¹³ experiments (Table II) also indicate that carbon monoxide can be formed in this system from a formaldehyde intermediate. In addition it is clear that carbon dioxide also can arise from the same intermediate (values of the absolute yield of nitrous oxide and of carbon dioxide were not measured in these experiments). While these conclusions disagree with those reached on the basis of the O¹⁸ work reported earlier (3) the relative insensitivity of the present technique to errors caused by possible exchange over the hot copper oxide suggest that they are the more reliable. The value of the C¹³/C¹² ratio found in the oxides of carbon are lower than that of the added formaldehyde. This implies that some compound, presumably formaldehyde, which is produced in the system also acts as a precursor to the oxides of carbon.

It may be concluded from the present data that formaldehyde is not inert in this photooxidation system and that the oxides of carbon can be formed from the reactions of this compound.

If equations [5] and [6] represent the major sources of the oxides of carbon, then $R_{\rm CO}/R_{\rm CO_2} = k_5/k_6$. The data from 15 minutes to 55 minutes yield a value $k_5/k_6 = 3.7 \pm 0.1$, a value which is somewhat lower than that (~5) which can be deduced from similar data in the earlier work (3). A detailed mechanism has been suggested (7) for these reactions which involves the formation of HCO₃ radicals followed by isomerization to O=COOH and decomposition either to carbon monoxide and HO₂ radical or to carbon dioxide and an hydroxyl radical.

If, in addition to the assumption above, it is also valid to assume (a) that nitrous oxide and secondary nitrogen arise only from [2] and [3], and (b) that [2] and [3] represent the sole fates of $CH_2N_2CH_3$ radicals formed in [1], and [5] and [6] the sole fates of formyl

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radicals formed in [4], then it follows that $(R_{CO}+R_{CO2})[A]/\{(R_{N2})_{secondary}+R_{N2O}\}[F] = k_1/k_4$. Calculations based on the data of Table I give $k_1/k_4 = 212 \pm 10$ with no obvious trend with conversion. If A_1/A_4 is taken as unity approximately, this calculation indicates that $E_1 = E_4 = 4-5$ kcal/mole. Since it has not been established that the radical R in [1] and [4] is a single species (probably OH, HO_2 , CH_3O , and CH_3O_2 enter into these reactions at various rates), the value calculated cannot be ascribed to a single reaction. However, it might be noted that the difference obtained is relatively large compared with the difference $E_1 - E_4$ when R is a methyl radical. This latter difference has been reported as 2.2 kcal/mole (8).

Brief mention should be made at this point of the shape of the curve of the quantum yield of methanol as a function of conversion (Fig. 1). Analytical uncertainties are rather large in the low-conversion region and rigorous attention had to be paid to the purity of the reactants. The combination of these two factors renders the determination of quantum yields in this region highly imprecise. On the basis of the present data it is impossible to decide whether Φ_{CH_3OH} approaches unity or zero at these conversions (Fig. 1). While of obviously considerable significance, possible explanations of either extrapolation are closely associated with the mechanism of formation of methyl hydroperoxide recently found to be a product in this system (9). Detailed consideration of these points will be presented at a later time.

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REFERENCES

1. G. R. HOEY and K. O. KUTSCHKE. Can. J. Chem. 33, 496 (1955) 2. R. L. STRONG and K. O. KUTSCHKE. Ch. J. Chem. 33, 496 (1955)

3.

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G. K. HOEY and K. O. KUTSCHKE. Can. J. Chem. 33, 496 (1955).
R. L. STRONG and K. O. KUTSCHKE. Can. J. Chem. 37, 1456 (1959).
F. WENGER and K. O. KUTSCHKE. Can. J. Chem. 37, 1546 (1959).
D. J. LE ROY. Can. J. Research, B, 28, 492 (1950).
C. E. BRICKER and W. A. VAIL. Ind. Eng. Chem., Anal. Ed. 17, 400 (1945).
A. R. BLAKE and K. O. KUTSCHKE, Can. J. Chem. In press.
A. M. MAZKOVICH and L. F. FILIPPOVA. Zhur. Fiz. Khim. 31, 2649 (1957).
S. TOBY and K. O. KUTSCHKE. Can. J. Chem. 37, 672 (1959).
M. SHAHIN and K. O. KUTSCHKE. J. Phys. Chem. In press.

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