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Photolysis of Formaldehyde in the Presence of Nitric Oxide

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The photolysis of CH_2O has been studied in the absence and presence of NO from room temperature to 300 °C. In the photolysis of CH_2O alone, the CO and H_2 formation rates increase greatly with temperature. When NO is added, these rates vary and reach constant values with an increase in the amount of NO. These limiting rates are independent of the temperature to within the experimental error, in contrast to the rates observed for CH_2O alone. It is suggested that the limiting rate of CO formation corresponds to the sum of the rates of the two primary processes, the molecular and radical reactions, and that that of H_2 formation corresponds to the rate of the molecular process. For photolysis totally inhibited by NO, the rates of formation of CO, H_2, N_2, and N_2O were examined and a reaction mechanism is proposed which is consistent with that for the photosensitized reaction between hydrogen and nitric oxide previously studied in this laboratory.

The effect of the addition of nitric oxide on the pyrolysis of formaldehyde has been investigated in this laboratory and it was found that nitric oxide very effectively inhibits the radical chain process, while nitric oxide reacts with formaldehyde at high temperature forming CHO radicals.¹⁾ Thus, NO has both inhibitive and accelerative effects on the free radical process, rendering the elucidation of the overall reaction mechanism very difficult.

In the work reported here, the photolysis of CH_2O was investigated in the presence of NO at lower temperatures, for which the thermal reaction between NO and CH_2O is negligible and NO reacts only with radicals formed photochemically.

Experimental

Materials. Formaldehyde was prepared from paraformaldehyde. The method of preperation and purification are same as those in a previous paper.¹⁾ Nitric oxide was obtained from Takachiho Kagaku Co., Ltd. with a research-grade purity of 99.6%, and subjected to several trap-to-trap distillations.

Apparatus. The reaction was studied in a conventional static system, and was carried out in a cylindrical quartz vessel of 262 ml placed in an electric furnace, which was wrapped in asbestos and placed inside a cylindrical alminum collar 20 cm long and 9 cm in diameter with walls 1.6 cm thick, for the purpose of maintaining a constant temperature.

The light source was a medium pressure mercury arc. A glass filter was used to remove light of wavelength less than 2700 Å.

Procedure. Formaldehyde and nitric oxide were introduced into the vessel, which was maintained at the experimental temperature. For all experiments, the incident light intensity was the same. The photolytic products were separated by means of cold traps and a Toepler pump, and analyzed quantitatively by means of a gas chromatograph. The separation and analysis techniques are similar to those described in a previous paper.¹⁾

Results

The amounts of CO, H_2, N_2, and N_2O produced during the photolysis of CH_2O with NO were measured. A large amount of H_2O was found, but it was not measured. An unmeasurable amount of CO_2 was observed at room temperature. No methanol was detected, although it is important in the pyrolysis.

The yields of CO, H_2, N_2, and N_2O were measured at different reaction times during the uninhibited and inhibited photolysis. Some results are given in Fig. 1, which shows that the amount of each product increases linearly from the beginning of the photolysis. The initial rate of formation of each product, in all experiments, was determined by the amount produced after 10 min of photolysis.

Figure 2 shows the results of a series of runs carried out at a constant pressure of formaldehyde (100 Torr) and various pressures of NO (0—100 Torr) at (a) room temperature, (b) 100 °C, (c) 200 °C, and (d) 300 °C. On the other hand, Fig. 3 shows the effect of the CH_2O pressure (20—120 Torr) on the photolysis for a fixed amount of NO (50 Torr) at (a) 100 °C and (b) 200 °C.

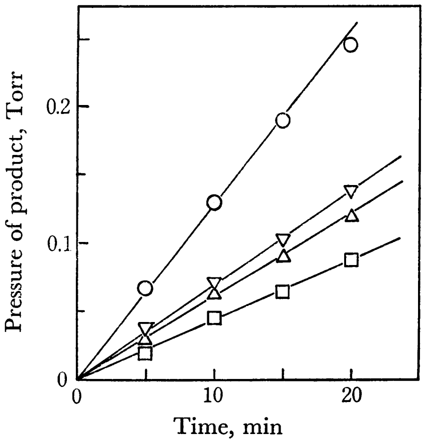

Fig. 1. Yields of products in the photolysis of 100 Torr CH_2O with 50 Torr NO at 100 °C.
○: CO, △: H_2, ▽: N_2, □: N_2O.

Discussion

The photodecomposition of CH_2O has been studied by a number of workers and it is well established that the photolysis occurs *via* two primary processes.²⁻⁴⁾

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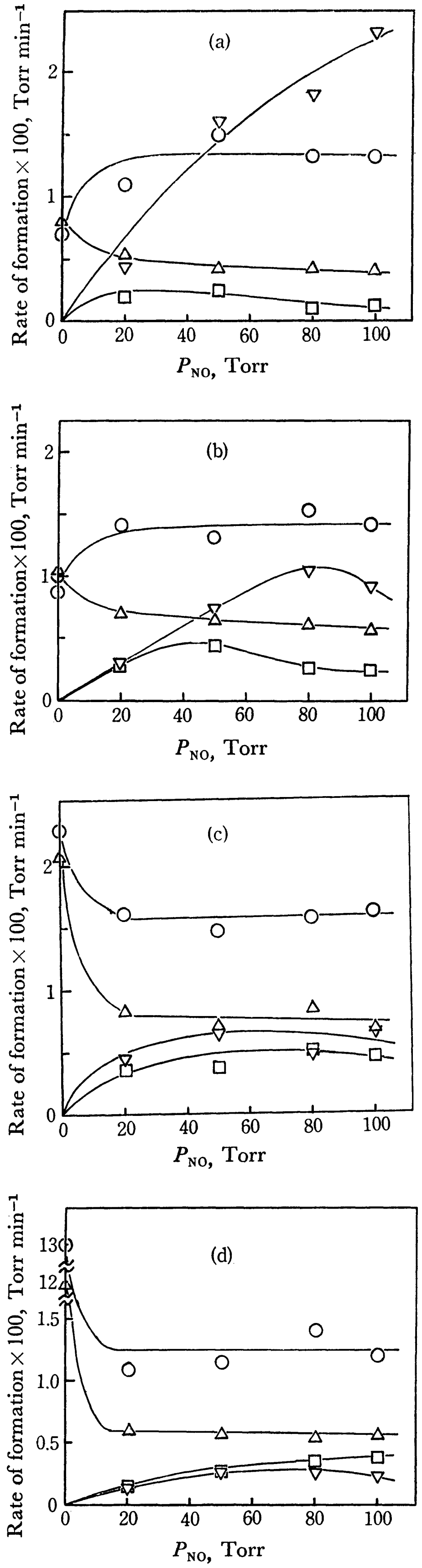

Fig. 2. Plot of rate of formation *vs.* NO pressure for the photolysis of 100 Torr CH_2O.
○: CO, △: H_2, ▽: N_2, □: N_2O.
(a) Room temperature, (b) 100°C, (c) 200°C, (d) 300°C.

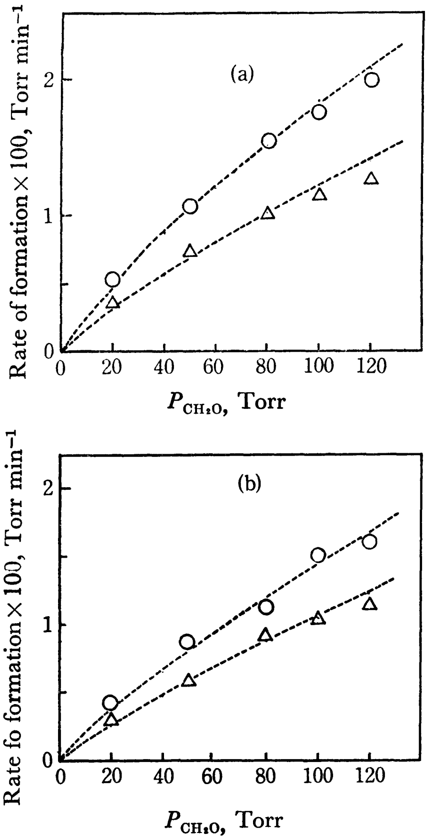

Fig. 3. Plot of rate of formation *vs.* CH_2O pressure for the photolysis with 50 Torr NO.
Data obtained were multiplied by factors in parentheses for the purpose of direct comparison with the dotted lines.
(a) 100°; ○: CO (1.35), △: H_2 (1.77).
(b) 200°, ○: CO (1), △: H_2 (1.5).

$$CH_2O + h\nu \longrightarrow H + CHO \qquad (I)$$

$$\longrightarrow H_2 + CO \qquad (II)$$

Sperling and Toby[4] observed that the quantum yields of the H_2 and CO formations do not vary with temperature between 80 and 120 °C. On the other hand, Akeroyd and Norrish,[2] and Calvert and Steacie[5] have found the quantum yield of CH_2O photolysis to increase with temperature at high temperatures, *e.g.*, $\phi_{CO}=1.0$ at 101 °C, 5.4 at 196 °C, and 69 at 295 °C.[5] In this work, the results shown in Fig. 2 (NO=0 Torr) indicate that the rates of H_2 and CO formation increase with temperature in a manner similar to that observed by them. Such a temperature dependency of the quantum yields, together with the fact that nearly equal amounts of H_2 and CO are produced in the photolysis indicates that Process I is followed by the chain process, which is assumed to proceed mainly *via* the following reactions:

$$H + CH_2O \longrightarrow H_2 + CHO$$

$$CHO + M \longrightarrow CO + H + M$$

$$CHO + (wall) \longrightarrow products + (wall)$$

When NO is added to the CH_2O during photolysis, the rates of CO and H_2 formation vary and attain limiting values for increasing amounts of NO, as is shown in Fig. 2. The limiting rates of CO and H_2

formation are approximately independent of the temperature, contrary to those for the photolysis of CH_2O alone.

Since, in the CH_2O pyrolysis, H_2 formation is almost totally inhibited by a small amount of NO, the rate of H_2 formation which occurs for photolysis with NO added can be attributed to the molecular Process II. The difference between the limiting rates of the CO and H_2 formations should be regarded as the rate of CO formation caused by Process I. The following discussion will, therefore, concern the radical process caused by Reaction I under conditions of sufficient inhibition by NO ($P_{NO}>30$ Torr).

The Hg-photosensitized reaction of H_2 and NO[6] has been studied in this laboratory in order to study the reactions in a system containing H atoms and NO at low temperature. In this photosensitization, it was found that the main products are H_2O and N_2, with the H_2O formation being of the zeroth order and the N_2 formation of the first order with respect to NO at room temperature. A third product is N_2O and its rate of formation decreases with the amount of NO. Although the amount of H_2O in the products was not measured in the work reported here, stoichiometry predicts that

$$R_{CO} - R_{H_2} = R_{H_2O}$$

i.e., the same amounts of CO and H_2O are formed by the radical process. The reaction orders of the H_2O, N_2, and N_2O formations with respect to NO are quite similar both for H_2–NO photosensitization and for the photolysis studied at room temperature, indicating that these products are formed by similar processes in both cases.

Thus, the following reaction scheme is proposed for the radical process of CH_2O–NO photolysis at room temperature, the scheme being consistent with that of H_2–NO photosensitization:

$$CH_2O + h\nu \longrightarrow CHO + H \tag{I}$$
$$CHO + M \longrightarrow CO + H + M \tag{1}$$
$$CHO + HO \longrightarrow CO + HNO \tag{2}$$
$$H + NO + M \longrightarrow HNO + M \tag{3}$$
$$2HNO \longrightarrow H_2O + N_2O \tag{4}$$
$$HNO + 2NO \longrightarrow N_2 + H + NO_3 \tag{5}$$
$$NO_3 + NO \longrightarrow 2NO_2 \tag{6}$$
$$NO_2 + HNO \longrightarrow OH + 2NO \tag{7}$$
$$OH + HNO \longrightarrow H_2O + NO \tag{8}$$

This reaction scheme leads to the following rate equations:

$$R_{CO} = R_1 + R_2 = I_{a(I)}$$
$$R_{H_2O} = R_4 + R_8 = I_{a(I)},$$

where $I_{a(I)}$ refers to the rate of the primary Reaction I.

The extinction coefficient of CH_2O has been estimated to be $\varepsilon=4.84$,[4] 1.87,[4] and 0.07[7] mol^{-1} l cm^{-1} at 313, 334, and 366 nm, respectively. In Fig. 3, the dotted lines are drawn since the rate is proportional to the intensity of light absorbed by CH_2O using the value of the extinction coefficient given above at 313 nm. Although the curvatures of the observed values are larger than those calculated, the differences are not as large. Thus, Figs. 2 and 3 show that R_{CO} and R_{H_2O} in the radical process ($=R_{CO(total)}-R_{H_2}$) are proportional to I_a and are independent of the NO pressure, supporting the above rate equations.

According to the above reaction scheme, N_2 is produced by the chain disproportionation of NO, Reactions 5 and 3,[8] and N_2O is produced by the disproportionation of HNO, Reaction 4.[9] Hence,

$$R_{N_2} = k_5[HNO][NO]^2$$
$$R_{N_2O} = k_4[HNO]^2,$$

where [HNO] can be obtained from the following equation

$$I_{a(I)} = k_4[HNO]^2 + k_7[NO_2][HNO].$$

As discussed in a previous paper on H_2–NO photosensitization,[6] the following relations hold if $R_4 \ll R_7(=R_8)$** and $[NO_2] \propto [NO]$***, NO_2 being consumed by reaction with Hg in the reaction cell, the amount of which it is not possible to measure accurately:

$$R_{N_2} \propto I_a[NO]$$
$$R_{N_2O} \propto I_a^2/[NO]^2$$

Figure 2(a) indicates that these relations are approximately valid at room temperature.

At higher temperatures, however, the above rate expressions for N_2 and N_2O do not hold as is shown in Figs. 2(b), (c), and (d). As the temperature rises up to 200 °C, moreover, R_{N_2} decreases and R_{N_2O} increases, with the latter decreasing for temperatures above 200 °C. Such dependencies on the temperature were also observed for H_2–NO photosensitization and can be explained by a similar reaction mechanism. Since Reaction 5 is a termolecular reaction, its rate should decrease for a rise in temperature, causing a decrease of R_{N_2}. The increase of R_{N_2O} with the temperature increase is assumed to be caused by the following reaction:

$$HNO + NO \longrightarrow N_2O + OH \tag{9}$$

in addition to Reaction 4, which appears to have a small activation energy and a rate that should not depend greatly on the temperature. At temperatures higher than 200 °C, the following reaction will proceed:

$$2HNO \longrightarrow 2OH + N_2 \tag{10}$$

Thus, a great amount of HNO is consumed by Reactions 10 and 8, with the R_{N_2O} being decreased by Reactions 4 and 9. The relations $R_{CO}=I_{a(I)}$ and $R_{H_2O}=I_{a(I)}$, however, are valid even for the reaction scheme at high temperature.

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** This assumption is reliable because the N_2O yield is much smaller than that of H_2O at room temperature (Fig. 2(a)).

*** Since NO_2 is produced by chain disproportionation of NO, and its rate determining step should be (5), this assumption seems not to be very unprobable.

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