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The Thermal Reaction of Hydrogen and Nitric Oxide

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The kinetics of the H_2–NO pyrolysis was studied at 400 °C; the reaction was found to be first-order in H_2 and to be independent of NO. It is suggested that the reaction proceeds by means of a free-radical chain mechanism: $H_2+NO(surface)\rightarrow HNO+H(1)$, $H+NO\rightleftharpoons HNO$ (2), $2HNO\rightarrow 2OH+N_2$ (3), $OH+H_2\rightarrow H_2O+H(4)$ and $2HNO\rightarrow H_2O+N_2O(5)$. This reaction scheme resembles that proposed for the CH_2O–NO pyrolysis at 500 °C except for the initiating step (1), which takes place on the wall of the vessel in the H_2–NO pyrolysis.

In this laboratory, the effect of nitric oxide on formaldehyde pyrolysis has been studied at 500°C.[1] As the H atom, in the chain decomposition of formaldehyde, is a chain carrier, it is desirable to know the reaction of a system containing H and NO in order to elucidate the above reaction. In order to follow the H_2–NO reaction, the H–NO reaction has been investigated by several workers; Hinshelwood and Mitchell in the range of 700°—805 °C,[2] Graven at 850°—1060 °C,[3] Kaufman and Decker at 900°—1152 °C,[4] and recently Wilde at 800°—1060 °C.[5] Wilde presented the following scheme:

$$H_2 + NO \rightleftharpoons HNO + H$$
$$HNO + NO \longrightarrow N_2O + OH$$
$$OH + H_2 \longrightarrow H_2O + H$$
$$H + NO + M \rightleftharpoons HNO + M$$
$$(2HNO \longrightarrow N_2O + H_2O)$$

No work, however, has been reported on the H_2–NO reaction below 500 °C. In this work, the kinetics of the H_2–NO pyrolysis has been studied mainly at 400 °C, and a reaction scheme has been derived.

Experimental

Materials. The nitric oxide and hydrogen used were obtained from the Takachiho Kagaku Co., Ltd., in research-grade purities of 99.6% and 99.95% respectively. They were used without further purification.

Apparatus. The apparatus used in the present work was similar to that described previously.[1] Two cylindrical vessels were used: an unpacked quartz one of 262 cm^3, with a S/V ratio of 0.83 cm^{-1}, and a packed Pyrex one of 124 cm^3, with a S/V ratio of 11.3 cm^{-1}.

Procedure. The required quantities of hydrogen and nitric oxide were introduced into the vessel, which had been kept at the experimental temperature. The products of decomposition were then separated and collected by means of cold traps and a Toepler gauge, and analysed quantitatively by means of a gas chromatograph.

Water, one of the product, was converted to hydrogen by treating it with the sodium evaporated onto the surface of a glass trap as a thin layer; then its amount was determined, though the measurement was not very accurate. Except for the case of water, the analytical technique used was similar to that described previously.[1]

Results

The products detected in the thermal reaction of the H_2–NO system are nitrogen, nitrous oxide, and water. Figure 1 shows the temperature dependence of each product after a pyrolysis of two hours at temperatures ranging from 20° to 500 °C.

Figures 2 and 3 show the effects of the nitric oxide and hydrogen pressures respectively on each product formation in the thermal reaction at 400 °C. Figures 4 and 5 show the dependences of the nitrogen and nitrous oxide formations in the packed vessel at 400 °C on the nitric oxide and hydrogen pressures respectively. Figures 2—5 demonstrate that the formation of nitrogen is first-order in relation to hydrogen and zero-order in relation to nitric oxide in both the unpacked and packed vessels, while that of nitrous oxide obeys a

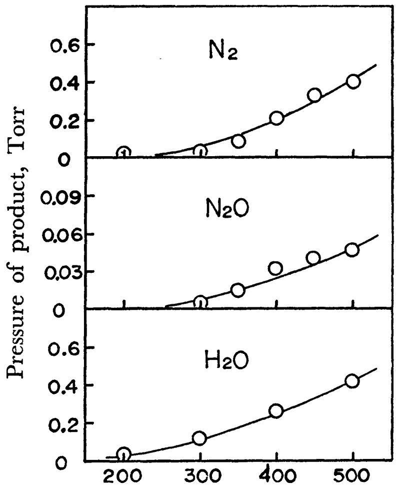

Fig. 1. Temperature dependences of product amounts for the pyrolyses of 50 Torr H_2 and 50 Torr NO in the unpacked vessel for 2 hr.

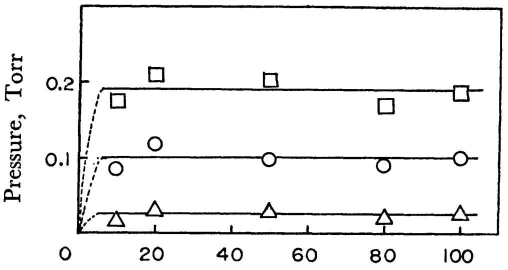

Fig. 2. Plot of amount of product *vs.* NO pressure for the pyrolysis of 20 Torr (fixed) H_2 and NO in the unpacked vessel at 400°C for 2 hr.
□: H_2O, ○: N_2, △: N_2O

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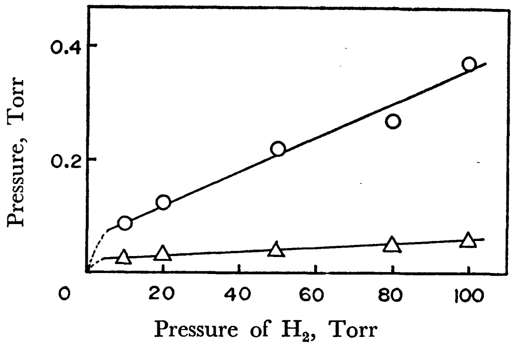

Fig. 3. Plot of amount of product *vs.* H_2 pressure for the pyrolysis of 20 Torr (fixed) NO and H_2 in the unpacked vessel at 400°C for 2 hr.
○: N_2, △: N_2O

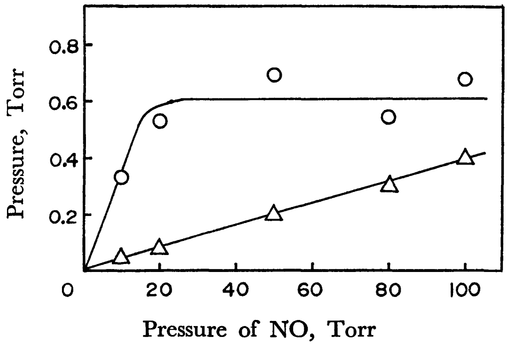

Fig. 4. Plot of amount of product *vs.* NO pressure for the pyrolysis of 20 Torr (fixed) H_2 and NO in the packed vessel at 400°C for 2 hr.
○: N_2, △: N_2O

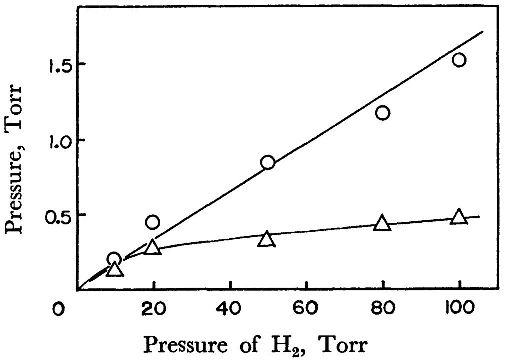

Fig. 5. Plot of amount of product *vs.* H_2 pressure for the pyrolysis of 80 Torr (fixed) NO and H_2 in the packed vessel at 400°C for 2 hr.
○: N_2, △: N_2O

different rate low in each vessel. (The amount of water was not determined in the packed vessel.)

Discussion

As is indicated in Fig. 1, the H_2–NO reaction begins to occur at about 300 °C and is accelerated as the temperature increases within the range employed. The facts that the H_2–NO reaction begins to occur at a relatively low temperature and that the main reactions, by which water and nitrogen are formed, are not dependent on the nitric oxide pressure (Fig. 2) predict that an initiation reaction is the surface reaction. This suggestion is confirmed by the results in the packed vessel (Figs. 4 and 5), *i.e.*, the rate of the formation of nitrogen, one of the main products, is increased by the increase in the S/V ratio compared with that in the unpacked vessel (Figs. 2 and 3), even though the rate law is not changed.

In the present laboratory, the pyrolysis of formaldehyde with nitric oxide has been studied at 500 °C; we obtained this stoichiometric relation:1)

$$CH_2O + NO \longrightarrow CO + H_2O + (1/2)N_2$$

though it is very rough. In the present work, a similar rough stoichiometry seems to hold:

$$H_2 + NO \longrightarrow H_2O + (1/2)N_2$$

On the other hand, different rate laws are observed in each pyrolysis: *i.e.*, in the CH_2O pyrolysis, it is:

$$-d[CH_2O]/dt = k[CH_2O][NO]$$

while in the H_2 pyrolysis it is:

$$-d[H_2]/dt = k[H_2]$$

with a sufficient amount of NO being present in each case.

The facts hitherto presented suggest a chain mechanism of the H_2–NO pyrolysis, which consists of a different initiating step and of consequent steps analogous to those proposed in the CH_2O–NO pyrolysis:1)

$$H_2 + NO(\text{surface}) \longrightarrow HNO + H \tag{1}$$

$$H + NO + M \rightleftharpoons HNO + M \tag{2}$$

$$2HNO \longrightarrow 2OH + N_2 \tag{3}$$

$$OH + H_2 \longrightarrow H_2O + H \tag{4}$$

$$2HNO \longrightarrow H_2O + N_2O \tag{5}$$

In this scheme, Reaction (1) is the chain-initiating step, (2), (3), and (4) are the chain-carrying steps, and (5) the chain-ending step. Reaction (1) is proposed because of the surface effect on this reaction and the independency of the rate in relation to the NO pressure. Reaction (3) has been proposed in the study of the CH_2O–NO pyrolysis1) and suggested to be faster than (5) at 500 °C.

Making the usual steady-state assumption of transient species (H, OH, and HNO), the above reaction scheme yields the following rate equation:

$$R_{N_2} = R_3 = (k_3/k_5)R_5 = (k_3/k_5)R_1$$

where R refers to the rate of the reaction shown by a suffix or that of the formation of the product shown by a suffix. If Reaction (1) is first-order in relation to H_2 and zero-order in relation to NO,

$$R_{N_2} = (k_1k_3/k_5)[H_2]$$

The value of k_1 should depend on the amount of the surface area. A similar treatment of the reaction scheme also yields this rate equation:

$$R_{H_2O} = R_4 + R_5 = 2R_3 + R_5$$

If the reaction chain is sufficiently long, R_5 may be neglected compared with R_3. Then

$$R_{H_2O} \simeq 2R_3 = 2R_{N_2}$$

These rate equations satisfy both the kinetics and the stoichiometry described above. The possibilities of the occurences of the other reactions were examined in a manner described in a previous work and so are omitted here; *cf* Table 1 in Ref. 1.

The above scheme also leads to this equation:

$$R_{N_2O} = k_1[H_2]$$

which is consistent with the results obtained in the unpacked vessel (Figs. 2 and 3). In the packed vessel, however, the rate of the N_2O formation does not follow this equation (Figs. 4 and 5). As another source of nitrous oxide, Reaction (6) may be presumed:

$$HNO + NO \longrightarrow N_2O + OH \qquad (6)$$

This reaction has been proposed in the temperature range of 800°—1060 °C[3] and has presumed to take place simultaneously with (5) in the CH_2O–NO pyrolysis at 500 °C.[1]

The rate of the N_2O formation due to (6) may be expressed as:

$$R_{N_2O(6)} = (k_1^{1/2}k_6/k_5^{1/2})[H_2]^{1/2}[NO]$$

This equation appears to agree with the results in the packed vessel (Figs. 4 and 5). Reaction (6) should have a heterogeneous nature at 400 °C, since N_2O seems to be formed predominantly by Reaction (6) in the packed vessel and by Reaction (4) in the unpacked vessel.

The occurrence of (6), in addition to (1)—(5), does not affect the rate equations of the N_2 and H_2O formations.

Reactions (7)[6] and (8)[7] have been proposed between nitroxyl and nitric oxide at lower temperatures:

$$HNO + 2NO \longrightarrow N_2 + H + NO_3 \qquad (7)$$

$$HNO + 2NO \longrightarrow HNO_3 + N_2 \qquad (8)$$

Reaction (7), followed by (2), causes the chain disproportionation of nitric oxide, which may be represented stoichiometrically as:

$$3NO \longrightarrow N_2 + NO_3$$

(Reaction (7) does not affect the rate of the formation of another product.) Reaction (7) has also been suggested, in the studies of CH_2O–NO photolysis[8] and H_2–NO photosensitization reaction[9] carried out in this laboratory, as taking place in the system containing hydrogen atoms and nitric oxide at lower temperatures. At 500 °C, however, the disproportionation of nitric oxide was indicated not to occur by the study of the CH_2O–NO pyrolysis.[1]

The rate of N_2 formation due to (7) may be represented as:

$$R_{N_2(7)} = (k_1^{1/2}k_7/k_5^{1/2})[NO]^2[H_2]^{1/2}$$

Reaction (7) does not seem to be as important as (3) as the N_2 source in the present conditions because of the disaccordance between the above rate equation and the rate law of N_2 formation observed, and also because of the failure to detect any NO_3 in the products.

Reaction (8) is also omitted, since (8) terminates the reaction chain; thus, the occurrence of this reaction alters the rate law of the main reaction. This has already been examined in a manner described previously.

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