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A Shock Tube Study on the Pyrolysis of Acetylene in the Presence of Nitrogen Oxide

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The pyrolysis of acetylene in the presence of nitrogen oxide has been investigated by use of a single-pulse shock tube in the temperature range 1100—1650 K. The hydrocarbons produced in the presence of nitrogen oxide were quite the same as those obtained from the pyrolysis of acetylene by itself. The yield-temperature plots of 1-buten-3-yne showed that at temperatures below 1350 K the formation rate of 1-buten-3-yne is reduced by the addition of nitrogen oxide. The retarding effect of nitrogen oxide on the 1-buten-3-yne formation was interpreted in terms of the reactions of nitrogen oxide with 1-ethynylvinyl and 2-ethynylvinyl radicals to yield propynenitrile and hydrogen cyanide, respectively. An illustrative radical chain mechanism was presented for the pyrolysis of acetylene in line with the experimental results obtained from the pyrolysis inhibited by nitrogen oxide. The radical chain is initiated by the bimolecular reaction of acetylene, *viz.* $2C_2H_2 \rightarrow C_4H_3 + H$, ethynyl and 2-ethynylvinyl radicals being the chain carriers, where C_4H_3 is 1-ethynylvinyl radical.

Since the work by Staveley and Hinshelwood on the inhibiting effect of nitrogen oxide on the decomposition of hydrocarbons,[1] the technique of nitrogen oxide addition has been utilized to confirm the existence of chain processes in the systems of decomposing hydrocarbons.

Nitrogen oxide addition method was also applied to the pyrolysis of acetylene. Below 800 K the addition of nitrogen oxide to acetylene system inhibited the consumption of acetylene.[2,3] On the other hand, nitrogen oxide was found to have no effect on the pyrolysis of acetylene at *ca.* 2000 K.[4] It seems of interest to examine an inhibiting effect by nitrogen oxide on the pyrolysis of acetylene at intermediate temperatures.

Hardly any analysis of reaction products containing nitrogen and oxygen atoms has been made in pyrolysis experiments. Sherwood and Gunning investigated the mercuryphotosensitized decomposition of acetylene in the presence of nitrogen oxide by the analysis of the reaction products involving nitrogen and oxygen atoms. From their study on the substituted vinyl radical reactions with nitrogen oxide, they concluded that a radical mechanism is operative in the system.[5,6]

Analysis of the inhibiting effect of nitrogen oxide on the pyrolysis products together with that of the reaction products containing nitrogen and oxygen atoms will make it possible to identify the substituted vinyl radicals assumed in the radical chain mechanism.[7]

Experimental

Apparatus and Procedure. The apparatus and procedure were essentially the same as those described in previous papers.[7-9] A 4-cm single-pulse shock tube was used, the driven section being 277 cm and the driver section 128.5 cm in length. The ultimate vacuum was *ca.* 6.4×10^{-5} Torr, the leak plus outgassing rate being *ca.* 1.5×10^{-5} Torr/min. Prior to the introduction of gases under investigation into the driven section, the tube was flushed with argon several times. Helium was used as a driver gas. Shocks were fired within five minutes after the driven section had been filled with gases.

Materials. Seven mixtures were prepared in a glass vessel of 10-l volume with the ratios $C_2H_2/NO/Ar = 10/0.2/89.8$; 10/1/89; 10/2/88; 5/1/94; 5/2/93; 1/1/98; and $C_2H_2/Ar = 10/90$. The gases were stirred with a glass fan located in the glass flask for at least four hours before use.

Nitrogen oxide (Matheson Co.) was purified at first by bulb-to-bulb distillation, and then passed through a silica gel column cooled with a Dry Ice–acetone bath.

The standard gas mixtures for the calibration of gas chromatography were the same as those used in the pyrolysis experiments. Carbon monoxide (research grade, Matheson Co.) was used.

Hydrogen cyanide was generated in a vacuum by pouring concd sulfuric acid onto potassium cyanide powder.[10] The crude hydrogen cyanide was purified by bulb-to-bulb distillation at *ca.* −50 °C.

Propynenitrile (cyanoacetylene) was prepared by the method of Moureu and Bongrand:[11]

$$\text{H-C}\equiv\text{C-COOCH}_3 \xrightarrow[-10\,^{\circ}\text{C}]{NH_4OH} \text{H-C}\equiv\text{C-CONH}_2$$

$$\xrightarrow[\text{vac. } 120\,^{\circ}\text{C}]{P_2O_5\text{, sand}} \text{H-C}\equiv\text{C-C}\equiv\text{N.}$$

Propynal (propiolaldehyde) was prepared from propynol.[12] Cyanogen was generated by pouring an aqueous sodium cyanide solution onto copper(II) sulfate pentahydrate at 50 °C, and dried by passing through diphosphorus pentaoxide.[13] Formaldehyde was prepared by the distillation of paraformaldehyde at *ca.* 120 °C. All the gases synthesized were purified by trap-to-trap distillation at Dry Ice–acetone temperature. The purified gases were diluted with argon gas and used as reference gases for gas-chromatographic analysis.

Analytical. The reaction products were analyzed by gas chromatography. The details of the hydrocarbon analysis were reported.[7] Propynenitrile, cyanogen, and propynal were analyzed in the same way as in the hydrocarbons. The order of elution was CH_4, C_2H_4, C_2H_2, allene, propyne, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, propynenitrile, cyanogen, and propynal at the temperature of 140 °C. The propynenitrile was identified by gas-chromatographic comparison with the synthesized gas. Cyanogen, however, has the same retention time as that of propynenitrile at 140 °C. Thus propynenitrile cannot be seperated from cyanogen on a Porapak N column at other temperatures.

Hydrogen cyanide and formaldehyde were analyzed at 60 °C on a 3 mm × 0.8 m column packed with Porapak Q using helium ionization detector. When water is contained in the test gas and shock heated sample gas, it interferes with the analysis of hydrogen cyanide and formaldehyde. However, neither sample gas nor the shock heated gas contained water in detectable amounts. Carbon monoxide was analyzed at room temperature with a thermal conductivity cell, on a 1.2 m column packed with molecular sieve 13 X(80—100 mesh). Carbon monoxide appeared at the tail end of the nitrogen oxide peak, but no difficulty was encountered in the analysis, analytical error being larger at low concentration of carbon monoxide in the shock heated gas.

Results

The mixtures were subjected to shock heating in the temperature range 1100—1650 K. The total densities behind the reflected shock waves were *ca.* 2.67×10^{-5} mol/cm^3, the reaction times being *ca.* 900 μs. The shock heated samples were extracted into evacuated bulbs of 60 ml volume, and analyzed by gas chromatography.

Product analyses for the hydrocarbons produced in the presence and absence of nitrogen oxide showed that the hydrocarbons formed in the C_2H_2–NO system and in the C_2H_2–Ar system are quite the same; CH_4, C_2H_4, C_2H_6, allene, propyne, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, and benzene being generated. The major products were also 1-buten-3-yne, 1,3-butadiyne and hydrogen in the presence of nitrogen oxide, the shapes of their yield-temperature plots being similar to those in the absence of nitrogen oxide. The minor products were CH_4, C_2H_4, allene, propyne, and benzene, trace products being C_2H_6 and 1,3-butadiene as in the case of the pyrolysis of acetylene alone.

Besides the hydrocarbons, hydrogen cyanide and carbon monoxide were formed as the major products containing nitrogen and oxygen atoms in the temperature range studied. Propynenitrile was found in much smaller amounts. No other products containing nitrogen and/or oxygen atoms such as N_2, N_2O, CO_2, O_2, and H_2O were found in large amounts. Since the amount of carbon monoxide was approximately equal to that of hydrogen cyanide (Fig. 1), there would be no missing products involving nitrogen and oxygen atoms. Thus the amount of nitrogen oxide consumed in the pyrolysis should be nearly equal to the yields of carbon monoxide and hydrogen cyanide.

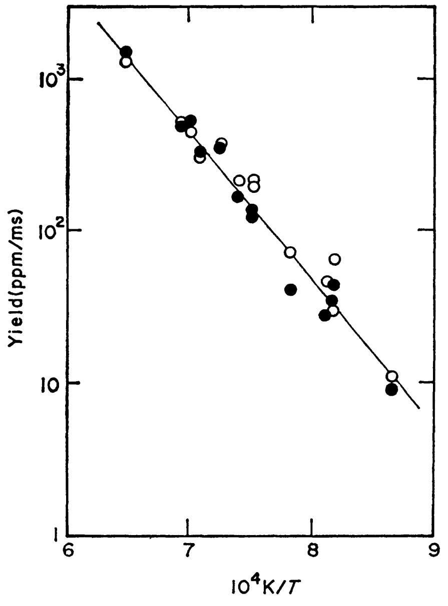

Fig. 1. Yields of carbon monoxide and hydrogen cyanide as a function of temperature (C_2H_2/NO/Ar=10/2/88). ●: Carbon monoxide, ○: hydrogen cyanide.

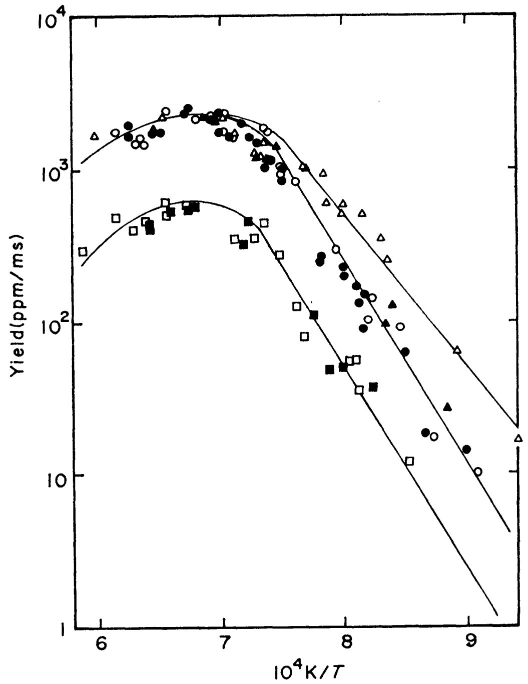

Fig. 2. Effect of nitrogen oxide on the rate of 1-buten-3-yne formation.
△: C_2H_2/Ar=10/90, ▲: C_2H_2/NO/Ar=10/0.2/89.8, ○: C_2H_2/NO/Ar=10/1/89, ●: C_2H_2/NO/Ar=10/2/88, □: C_2H_2/NO/Ar=5/1/94, ■: C_2H_2/NO/Ar=5/2/93.

Inhibited Rate of 1-Buten-3-yne Formation. The yields of 1-buten-3-yne for five mixtures with different composition of C_2H_2 and NO are plotted as a function of temperature in Fig. 2. The yield-temperature plots of 1-buten-3-yne show that at temperatures below 1350 K the yield decreases with the addition of nitrogen oxide, and that above 1350 K the yield is almost the same as that in the C_2H_2–Ar system. The rates of 1-buten-3-yne formation are also of second-order with respect to acetylene, and depend little on the amount of nitrogen oxide added at both lower and higher temperatures. The decrease in the yield of 1-buten-3-yne at lower temperatures can be attributed to the inhibition by nitrogen oxide added. An apparent second-order rate constant for the inhibited 1-buten-3-yne formation at temperatures below 1350 K was derived from 38 experiments by the least-squares method:

$$k_1(\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = (4.5\pm2.4)\times10^{15}\exp\{(-55700\pm2100)^{*}/RT\} \quad (1)$$

the errors denoting the standard deviation of the least-squares method. The Arrhenius plot of the second-order rate constants is shown in Fig. 3. The frequency factor in k_1 is considerably greater than that in the normal second-order rate constant.

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[*] The activation energy is expressed in cal/mol (1 cal_{th} = 4.184 J).

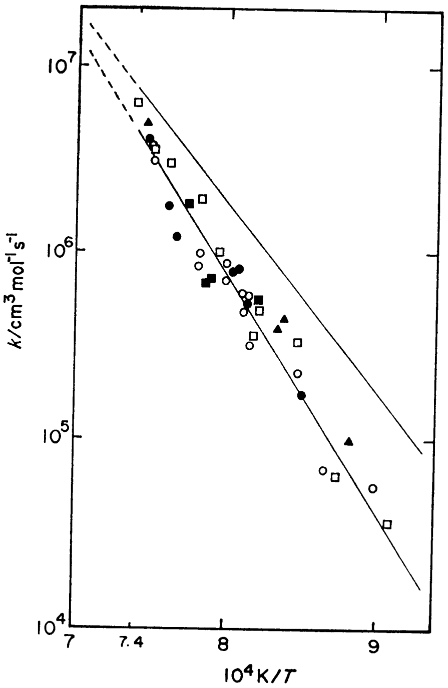

Fig. 3. Arrhenius plots of the second-order rate constants for 1-buten-3-yne formation inhibited by nitrogen oxide, the upper straight line showing the second-order rate constant obtained previously.[7)]
▲: C_2H_2/NO/Ar=10/0.2/89.8, ○: C_2H_2/NO/Ar=10/1/89, ●: C_2H_2/NO/Ar=10/2/88, □: C_2H_2/NO/Ar=5/1/94, ■: C_2H_2/NO/Ar=5/2/93.

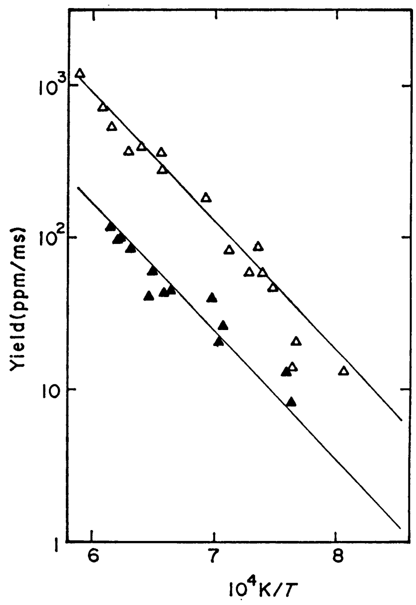

Fig. 5. Dependence of hydrogen cyanide formation rate on acetylene concentration.
△: C_2H_2/NO/Ar=5/1/94, ▲: C_2H_2/NO/Ar=1/1/98.

Rate of Hydrogen Cyanide Formation. Simultaneously with the reduction of 1-buten-3-yne yield, hydrogen cyanide and carbon monoxide were formed in approximately equal amounts. In order to determine the concentration dependence of hydrogen cyanide formation on acetylene and nitrogen oxide, the yields of hydrogen cyanide for four mixtures, *viz.* C_2H_2/NO/Ar=10/0.2/89.9; 10/1/89; 5/1/94; and 1/1/98; are plotted against temperature in Figs. 4 and 5. We see that the rate of hydrogen cyanide formation is nearly of first-order in both acetylene and nitrogen oxide. An apparent second-order rate expression was fitted to the data (61 points obtained from the shock heated mixtures of C_2H_2/NO/Ar=10/0.2/89.8; 10/1/89; 10/2/88; 5/1/94; and 1/1/98) by the least-squares method:

$$k_2(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = (5.4\pm1.6) \times 10^{12} \exp\{(-37700\pm1300)/RT\}. \quad (2)$$

The Arrhenius plot of the second-order rate constants

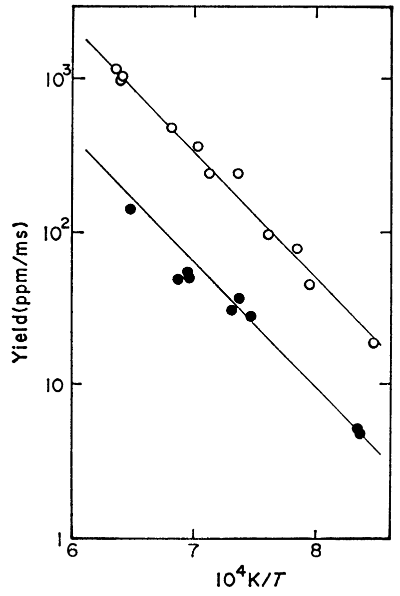

Fig. 4. Dependence of hydrogen cyanide formation rate on nitrogen oxide concentration.
○: C_2H_2/NO/Ar=10/1/89, ●: C_2H_2/NO/Ar=10/0.2/89.8.

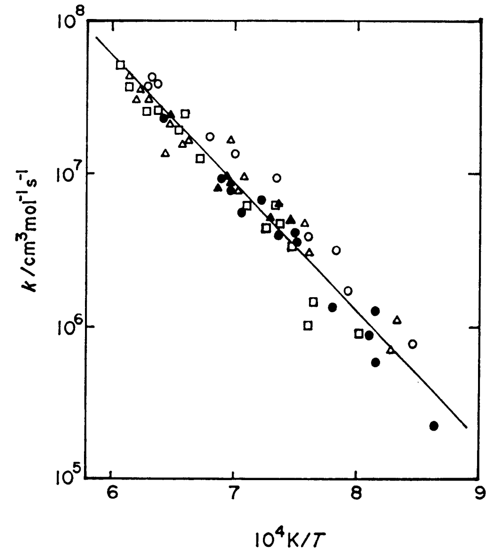

Fig. 6. Arrhenius plots of the second-order rate constants for hydrogen cyanide formation.
▲: C_2H_2/NO/Ar=10/0.2/89.8, ○: C_2H_2/NO/Ar=10/1/89, ●: C_2H_2/NO/Ar=10/2/88, □: C_2H_2/NO/Ar=5/1/94, △: C_2H_2/NO/Ar=1/1/98.

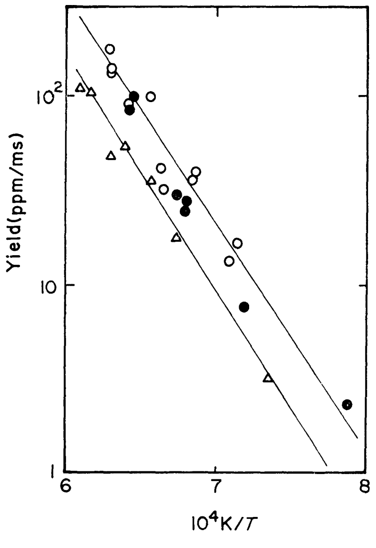

Fig. 7. Dependence of propynenitrile formation rate on acetylene and nitrogen oxide concentrations.
○: $C_2H_2/NO/Ar=10/1/89$, ●: $C_2H_2/NO/Ar=5/2/93$, △: $C_2H_2/NO/Ar=5/1/94$.

is shown in Fig. 6. Hydrogen cyanide and carbon monoxide continue to increase in the temperature range studied, whereas the yield of 1-buten-3-yne reaches its maximum at *ca.* 1500 K with a subsequent decrease.

Rate of Propynenitrile Formation. Propynenitrile was found at slightly higher temperatures and in smaller amounts than hydrogen cyanide. In determing the concentration dependence of acetylene and nitrogen oxide, the data obtained from the runs for the mixtures of $C_2H_2/NO/Ar=10/1/89$; 5/1/94; and 5/2/93 were adopted, since the yields of propynenitrile for the mixtures of $C_2H_2/NO/Ar=10/0.2/89.8$ and 1/1/98 were very small, involving large error. The rates of propynenitrile formation as a function of temperature are plotted in Fig. 7. The rate of propynenitrile generation is of the second-order with respect to acetylene. Although the data obtained from the runs for the mixture of $C_2H_2/NO/Ar=5/2/93$ scatter considerably, the rate of propynenitrile formation is expected to be also of the first-order with respect to nitrogen oxide by analogy with that of hydrogen cyanide production. An apparent second-order rate constant was derived by the least-squares method:

$$k_3(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = (9.9\pm2.3)\times10^{13}\exp\{(-53300\pm2500)/RT\}. \quad (3)$$

For derivation, only the data in Fig. 7 (25 points) were adopted. The Arrhenius plot of the second-order rate constants is shown in Fig. 8.

Effects on the Other Products. The influence of added nitrogen oxide on the formation of hydrogen is illustrated in Fig. 9. The shape of yield-temperature plots for hydrogen is similar to that in the absence of nitrogen oxide. The yield of hydrogen increases considerably at higher temperatures, and appears to depend little on the concentration of nitrogen oxide added. The same is true for the yield-temperature plots of the other major and minor products.

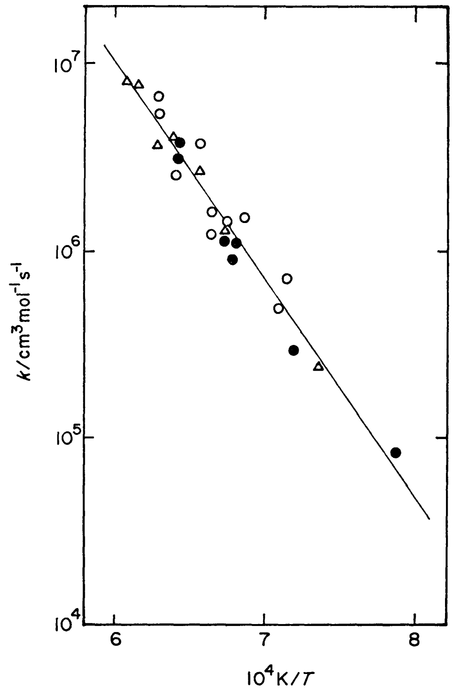

Fig. 8. Arrhenius plots of the second-order rate constants for propynenitrile formation.
○: $C_2H_2/NO/Ar=10/1/89$, ●: $C_2H_2/NO/Ar=5/2/93$, △: $C_2H_2/NO/Ar=5/1/94$.

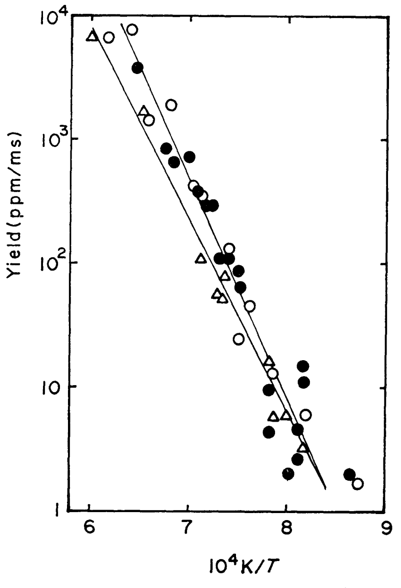

Fig. 9. Effect of nitrogen oxide on the yield of hydrogen.
△: $C_2H_2/Ar=10/90$, ○: $C_2H_2/NO/Ar=10/1/89$, ●: $C_2H_2/NO/Ar=10/2/88$.

Discussion

The same reaction product formation as in the absence of nitrogen oxide and similar shapes of the yield-temperature plots suggest that a similar mechanism is operative for the formation of the hydrocarbons in the C_2H_2–NO system. A mechanism for the pyrolysis of acetylene in the absence of nitrogen oxide was proposed from a thermochemical point of view:[7)]

$$2C_2H_2 \longrightarrow C_4H_3 + H, \tag{4}$$

$$C_4H_3 + C_2H_2 \longrightarrow C_6H_5, \tag{5}$$

$$C_6H_5 + C_2H_2 \longrightarrow C_4H_4 + C_4H_3, \tag{6}$$

$$H + C_2H_2 \longrightarrow C_2H_3, \tag{7}$$

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_4 + H, \tag{8}$$

$$2C_6H_5 \longrightarrow \text{termination}, \tag{9}$$

$$2C_2H_3 \longrightarrow \text{termination}, \tag{10}$$

where C_4H_3 radical is supposed to be 1-ethynylvinyl ($H_2C{=}\dot{C}{-}C_2H$) radical. Hereafter 1-ethynylvinyl and 2-ethynylvinyl($C_2H{-}CH{=}\dot{C}H$) radicals will be denoted by $C_4H_3(1)$ and $C_4H_3(2)$, respectively.

Initiation Step. Probable initiation steps for the radical chain mechanism of the pyrolysis of acetylene alone are as follows:

$$2C_2H_2 \longrightarrow C_4H_3(1) + H, \quad \Delta H^\circ = 46.2, \tag{4}$$

$$\longrightarrow C_4H_3(2) + H, \quad \Delta H^\circ = 67.1, \tag{11}$$

$$\longrightarrow C_2H_3 + C_2H, \quad \Delta H^\circ = 65.3. \tag{12}$$

In the presence of nitrogen oxide the abstraction reaction of H atom by nitrogen oxide could also be a probable initiation step:

$$C_2H_2 + NO \longrightarrow C_2H + HNO, \quad \Delta H^\circ = 62.0. \tag{13}$$

In the calculation of the heats of reaction, the heats of formation are based on the observed or estimated values.[14] At present stage, Reaction 4 is the most probable initiation step in view of the heat of reaction. Another probable initiation is the bimolecular reaction of nitrogen oxide when added in a large amount:

$$2NO \longrightarrow N_2O + O, \quad \Delta H^\circ = 36.0. \tag{14}$$

The rate constants of Reactions 4 and 14 are estimated to be[7,15]

$$k_4(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 3.5\times 10^{13} \exp(-47400/RT), \tag{15}$$

$$k_{14}(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 1.3\times 10^{12} \exp(-63800/RT). \tag{16}$$

The rate constant of Reaction 14 is much smaller than that of Reaction 4 in the temperature range studied. Thus Reaction 4 is the most predominant initiation step in the C_2H_2–NO system.

Mechanism of 1-Buten-3-yne Formation. The reduction of 1-buten-3-yne formation rate at temperatures below 1350 K is accompanied by the formation of hydrogen cyanide and carbon monoxide. No other products containing nitrogen and/or oxygen atoms are found except for the propynenitrile in much smaller amount. It seems likely that the hydrogen cyanide and carbon monoxide in nearly equal amounts are produced simultaneously or *via* the same intermediate. We have tried to interpret the inhibiting effect of nitrogen oxide on 1-buten-3-yne formation by the reactions of nitrogen oxide with the chain carrier radicals present in the above pyrolysis mechanism.

Examination of the Proposed Mechanism for the Pyrolysis: Sherwood and Gunning showed experimentally that C_2H_3 and $C_4H_3(2)$ radicals react with nitrogen oxide to generate formaldehyde, propynal, and hydrogen cyanide.[5] In general the reaction between the substituted vinyl radical and nitrogen oxide can be written as

$$XYC{=}\dot{C}Z + NO \longrightarrow XYC{=}O + ZCN,$$

where X, Y, and Z are functional groups of hydrocarbons. Thus the radicals in the proposed mechanism are expected to react with nitrogen oxide as follows:

$$C_4H_3(1) + NO \longrightarrow H_2CO + C_2HCN, \quad \Delta H^\circ = -60.0, \tag{17}$$

$$C_6H_5 + NO \longrightarrow C_4H_3CHO + HCN, \tag{18}$$

$$H + NO \longrightarrow HNO, \quad \Delta H^\circ = -49.9, \tag{19}$$

$$C_2H_3 + NO \longrightarrow H_2CO + HCN, \Delta H^\circ = -76.6, \tag{20}$$

where C_6H_5 is assumed to have the structure of $H_2C{=}C(C_2H){-}CH{=}\dot{C}H$. In the present analysis, hydrogen cyanide and propynenitrile have been detected as compounds containing nitrogen atom. Accordingly, the substituted vinyl radicals scavenged by nitrogen oxide should be C_2H_3, $C_4H_3(1)$, and C_6H_5 radicals in the proposed scheme.

If the chain propagation of Reaction 7 and 8 were mainly responsible for the formation of 1-buten-3-yne, the same amount of H_2CO as that of HCN would be produced. Therefore, as in the absence of NO, nearly equal amounts of hydrogen and carbon monoxide would be produced by the reaction

$$H_2CO \longrightarrow H_2 + CO, \quad \Delta H^\circ = 1.3. \tag{21}$$

As shown in Figs. 1 and 9, the yield of hydrogen is smaller than that of carbon monoxide at lower temperatures. Tadasa *et al.* reported that in the pyrolysis of H_2CO with a large excess of NO at 773 K the amount of hydrogen is very small as compared with that of carbon monoxide; water and nitrogen are formed instead.[16] In the present experiments, however, no detectable amounts of water and nitrogen have been found in the shock heated samples. In any event the chain propagation step of Reactions 7 and 8 can be concluded to have minor importance in the formation of 1-buten-3-yne. The same result has been obtained from the analysis of the isotopic distributions of C_2H_2 and C_4H_4 in the mixtures of C_2H_2 and D_2.[8]

On the other hand, if the chain propagation process, $C_4H_3(1)$ and C_6H_5 radicals as the chain carriers, is predominant, propynenitrile along with hydrogen cyanide should be detected. This is the case in the present experiments. Applying the steady-state treatment to Reactions 4, 5, 6, and 9, the steady-state concentrations of $C_4H_3(1)$ and C_6H_5, $[C_4H_3(1)]_{ss}$ and $[C_6H_5]_{ss}$, are given approximately by

$$[C_4H_3(1)]_{ss}/[C_6H_5]_{ss} \cong k_6/k_5, \tag{22}$$

$$= 1.3\times 10^2 \exp(-16100/RT). \tag{22$'$}$$

The rate constants adopted are as follows:[7,17]

$$k_5(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 6.3\times 10^{11} \exp(-6500/RT), \tag{23}$$

$$k_6(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 7.9\times 10^{13} \exp(-22600/RT). \tag{24}$$

Equation 22′ would hold approximately even in the presence of nitrogen oxide, assuming the rate constants k_{17} and k_{18} have the same order of magnitude because of the similarity of both reactions. Thus the rates of propynenitrile and hydrogen cyanide formation could be expressed by

$$R_{\mathrm{C_2HCN}}/R_{\mathrm{HCN}} \simeq (k_{17}[C_4H_3(1)]_{ss}[NO])/(k_{18}[C_6H_5]_{ss}[NO]) \simeq [C_4H_3(1)]_{ss}/[C_6H_5]_{ss}. \tag{25}$$

However, the above rate ratio obtained experimentally was

$$R_{C_2HCN}/R_{HCN} = 18\exp(-15600/RT). \qquad (26)$$

The observed rate for the formation of propynenitrile is much smaller than that predicted from the above mechanism. The chain propagation step of Reactions 5 and 6 is open to question; Reaction 6 particularly seems uncertain. The validity of the above discussion is based on the reliability of the rate constants used.

Alternative Mechanism for the Pyrolysis: An alternative chain propagation process is as follows:[17]

$$C_2H + C_2H_2 \longrightarrow C_4H_3(2), \quad \Delta H^\circ = -44.8, \qquad (27)$$

$$C_4H_3(2) + C_2H_2 \longrightarrow C_4H_4 + C_2H, \quad \Delta H^\circ = 11.7. \qquad (28)$$

The reaction of $C_4H_3(2)$ with NO produces HCN by

$$C_4H_3(2) + NO \longrightarrow C_2HCHO + HCN. \qquad (29)$$

The C_2H radical is reported not to react with NO.[5] A fast conversion process of $C_4H_3(1)$ into $C_4H_3(2)$ or C_2H is essential for the above chain propagation step to be compatible with the most predominant initiation step, Reaction 4.

If the isomerization of $C_4H_3(1)$ to $C_4H_3(2)$ such as

$$C_4H_3(1) \longrightarrow C_4H_3(2), \quad \Delta H^\circ = 20.9 \qquad (30)$$

were fast enough, the equilibrium would be established at an early stage of the reaction, since the reverse reaction would also be fast. The equilibrium concentrations are dominated by the heat of reaction because of the small entropy change of Reaction 30. At the present temperatures the equilibrium concentration of $C_4H_3(1)$ should be greater than that of $C_4H_3(2)$. This implies that the yield of propynenitrile should also be greater than that of hydrogen cyanide, which conflicts with the present observation. Thus the direct conversion of $C_4H_3(1)$ into $C_4H_3(2)$ will be too slow to be the initiation step.

Another process is the conversion of $C_4H_3(1)$ into C_2H radical. The H atom abstraction reaction of $C_4H_3(1)$ from C_2H_2 is an ineffective path to generate C_2H radical in view of the heat of reaction:

$$C_4H_3(1) + C_2H_2 \longrightarrow C_4H_4 + C_2H, \quad \Delta H^\circ = 32.6. \qquad (31)$$

The following path seems most promissing. The addition of $C_4H_3(1)$ to C_2H_2 is much faster than Reaction 31 with the rate constant of k_5 (Eq. 23):

$$C_4H_3(1) + C_2H_2 \longrightarrow H_2C{=}C(C_2H){-}CH{=}\dot{C}H, \quad \Delta H^\circ = -20.5. \qquad (5)$$

A successive H atom shift and the C–C bond rupture will occur:

$$\begin{aligned} H_2C{=}C(C_2H){-}CH{=}\dot{C}H &\longrightarrow H\dot{C}{=}C(C_2H){-}CH{=}CH_2, \\ &\longrightarrow HC{\equiv}C{-}CH{=}CH_2 + C_2H, \\ &\qquad \Delta H^\circ = 53.1. \qquad (32) \end{aligned}$$

The radical chain mechanism of 1-buten-3-yne formation is completed by

$$2C_4H_3(2) \longrightarrow \text{termination}. \qquad (33)$$

Application of steady-state approximation to $C_4H_3(1)$, $C_4H_3(2)$, C_6H_5, and C_2H radicals gives the following equations:

$$R_{C_4H_4} = k_{28}(k_4/2k_{33})^{1/2}[C_2H_2]^2, \qquad (34)$$

$$[C_4H_3(1)]_{ss} = (k_4/k_5)[C_2H_2], \qquad (35)$$

$$[C_4H_3(2)]_{ss} = (k_4/2k_{33})^{1/2}[C_2H_2]. \qquad (36)$$

As in the mechanism previously proposed, the second-order rate of 1-buten-3-yne formation is also derived from the revised mechanism. The heat of reaction for Reaction 28 is smaller than the activation energy estimated for Reactions 6 and 8 (*ca.* 18—23 kcal/mol).[7] Consequently Reaction 28 is likely to occur as the alternative to Reaction 6 forming 1-buten-3-yne. Substituting the rate constants in the right-hand side of Eqs. 35 and 36 for estimated ones, the ratio of the two ethynylvinyl radicals is calculated. The rate constant k_{33} adopted is as follows:[7]

$$k_{33}(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 2.0\times 10^{12}. \qquad (37)$$

The estimated values of $[C_4H_3(1)]_{ss}/[C_4H_3(2)]_{ss}$,

$$[C_4H_3(1)]_{ss}/[C_4H_3(2)]_{ss} = 19\exp(-17200/RT), \qquad (38)$$

agrees with the observed value of R_{C_2HCN}/R_{HCN}. This suggests that the revised mechanism is most probable one for the formation of 1-buten-3-yne in the presence and absence of nitrogen oxide.

Mechanism of Inhibited Pyrolysis. A radical chain mechanism for the inhibited formation of 1-buten-3-yne will be set up to be in line with that for the pyrolysis of acetylene by itself. Propynenitrile was not distinguished from cyanogen by the gas-chromatographic analysis. Shock tube experiments showed that the secondary reaction of hydrogen cyanide and that with acetylene and nitrogen oxide can be ignored in the temperature range studied.[18] Thus the propynenitrile originates from the reaction of nitrogen oxide with acetylene.

The characteristic features of inhibited 1-buten-3-yne formation by nitrogen oxide can be explained by the following radical chain mechanism:

$$\begin{aligned} &2C_2H_2 \longrightarrow C_4H_3(1) + H, && (4) \\ &C_4H_3(1) + C_2H_2 \longrightarrow C_6H_5, && (5) \\ &C_4H_3(1) + NO \longrightarrow C_2HCN + H_2CO, && (17) \\ &C_6H_5 \longrightarrow C_4H_4 + C_2H, && (32) \\ &C_2H + C_2H_2 \longrightarrow C_4H_3(2), && (27) \\ &C_4H_3(2) + C_2H_2 \longrightarrow C_4H_4 + C_2H, && (28) \\ &C_4H_3(2) + NO \longrightarrow C_2HCHO + HCN, && (29) \\ &C_2HCHO \longrightarrow C_2H + CHO, && (39) \\ &CHO \longrightarrow CO + H \quad \Delta H^\circ = 28.6, && (40) \\ &2C_4H_3(2) \longrightarrow \text{termination}. && (33) \end{aligned}$$

Assuming the steady-state concentrations of the radicals in the above mechanism, we can derive

$$R_4 = 2R_{33} + (R_{29} - R_{39}). \qquad (41)$$

Here the small effect of NO with $C_4H_3(1)$ radical on the reduction of 1-buten-3-yne formation rate is neglected. In the absence of nitrogen oxide Eq. 41 is reduced to

$$R_4 = 2R_{33}. \qquad (41')$$

When the rate of Reaction 29 is greater than that of Reaction 39, the steady-state concentration of $C_4H_3(2)$ in the presence of nitrogen oxide ($[C_4H_3(2)]_{ss}^{NO}$) is lower than that in its absence ($[C_4H_3(2)]_{ss}$; the inhibition by nitrogen oxide occurs. The observed second-order rates with and without nitrogen oxide are directly proportional to the steady-state concentrations of $C_4H_3(2)$ radical present in the systems:[7]

$$[C_4H_3(2)]^{NO}_{ss}/[C_4H_3(2)]_{ss} = R^{NO}_{C_4H_4}/R_{C_4H_4}, \qquad (42)$$
$$= 18 \exp(-9300/RT). \qquad (42')$$

It is observed that the inhibited rates of 1-buten-3-yne formation are hardly affected by the amounts of nitrogen oxide added (Fig. 2). The attainment of "limiting rate" can be easily accounted for by the above mechanism. When the amount of nitrogen oxide is increased to some extent, the rate of propynal generation is accelerated by Reaction 29 to the same extent, and in turn by Reaction 39 the same amount of the C_2H radical is regenerated as that of $C_4H_3(2)$ radical scavenged by Reaction 29 at a definite temperature. The C_2H radical is quickly converted into $C_4H_3(2)$ radical by Reaction 27. Thus the steady-state concentration of the $C_4H_3(2)$ radical is not affected by further addition of nitrogen oxide at a definite temperature. The present results are in agreement with those obtained at lower temperatures by Cullis *et al.*[3]

With increase in temperature the rate of Reaction 39 increases up to that of Reaction 29. In this case (Eq. 41′) no inhibition occurs, the steady-state concentration of $C_4H_3(2)$ radical being the same as that in the absence of nitrogen oxide. Actually, however, the 1-buten-3-yne begins to decompose at around 1350 K. The yield-temperature plots of 1-buten-3-yne are almost the same as those in the C_2H_2–Ar system above 1350 K. This suggests that the radical concentrations relevant to its formation and decomposition remain unchanged in the presence of nitrogen oxide.

The rate of propynenitrile formation is given by

$$R_{C_2HCN} = k_{17}[C_4H_3(1)]_{ss}[NO]. \qquad (43)$$

Since the yields of propynenitrile are very small as compared with those of hydrogen cyanide, the steady-state concentration of $C_4H_3(1)$ can be approximated by Eq. 35. Equation 43 is then expressed by

$$R_{C_2HCN} = (k_4k_{17}/k_5)[C_2H_2][NO]. \qquad (43')$$

The rate expression of propynenitrile formation is the same in both inhibited and uninhibited regions. On the other hand, within the present errors the yield-temperature plots of hydrogen cyanide are fitted to a single straight line in the temperature range studied. For the sake of simplicity, the rate expression in the uninhibited region is extended to the inhibited region:

$$R_{HCN} = k_{29}[C_4H_3(2)]_{ss}[NO]$$
$$= k_{29}(k_4/2k_{33})^{1/2}[C_2H_2][NO]. \qquad (44)$$

Since Reaction 17 and 29 are of the same type, k_{17} and k_{29} are expected to be nearly equal. As shown by Eqs. 43 and 44, the steady-state concentrations are related to the observed rates:

$$[C_4H_3(1)]_{ss}/[C_4H_3(2)]_{ss} = R_{C_2HCN}/R_{HCN}. \qquad (45)$$

The validity of the discussion on the pyrolysis mechanism is verified under the above conditions. The agreement between the observed and calculated values (Eqs. 26 and 38) is excellent.

By a comparison with the observed rates for propynenitrile and hydrogen cyanide formation, k_{17} and k_{29} are estimated from Eqs. 43′ and 44, respectively:

$$k_{17}(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 1.8\times10^{12} \exp(-12400/RT), \qquad (46)$$
$$k_{29}(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 2.3\times10^{12} \exp(-14900/RT). \qquad (47)$$

The small inhibiting effect of NO with $C_4H_3(1)$ radical being neglected, k_{17} is compared with k_{29} obtained in the inhibited region. The activation energy and frequency factor have approximately equal values in k_{17} and k_{29}. In the derivation of Eq. 45 (analogously Eq. 25), k_{17} was assumed to be equal to k_{29}, which is supported by Eqs. 46 and 47. It is noteworthy that the observed second-order rate constant for propynenitrile generation (k_3) has higher activation energy than that of hydrogen cyanide (k_2), whereas the activation energy of k_{17} is nearly the same as that of k_{29}. As can be seen from Eqs. 43 and 44, the difference between k_2 and k_3 results from the fact that in the present radical chain mechanism the steady-state concentration of $C_4H_3(1)$ is related to that of $C_4H_3(2)$ such as Eq. 38. Gay *et al.*[20] and Bopp and Kern[21] detected C_4H_3 radical in the pyrolysis of acetylene at temperatures above 1700 K by use of a time-of-flight mass spectrometer. The C_4H_3 radical as detected with mass spectrometer at $m/e=51$, however, cannot be distinguished among the C_4H_3 radical isomers. On the contrary, the addition of nitrogen oxide revealed that the C_4H_3 radicals are $C_4H_3(1)$ and $C_4H_3(2)$, both radicals being responsible for the formation of 1-buten-3-yne. Reaction 4 was predicted to be the most predominant initiation step on the basis of the heat of reaction. Detection of propynenitrile formation upon the addition of nitrogen oxide would provide experimental support for the occurrence of Reaction 4 as the initiation step.

Formation Mechanism for the Other Products. No significant change appears in the shape of yield-temperature plots of hydrogen (Fig. 9) and other major and minor products with appreciable increase in their yields at higher temperatures. The formation reactions will be unaltered, whereas the concentrations of the radicals relevant to their formation would increase considerably by the addition of nitrogen oxide.

As to the major products, the hydrogen will be generated by

$$H + C_2H_2 \longrightarrow H_2 + C_2H, \qquad \Delta H^\circ = 7.7, \qquad (48)$$

and 1,3-butadiyne will be formed by

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H, \qquad \Delta H^\circ = -4.8. \qquad (49)$$

H and C_2H are not scavenged by nitrogen oxide. Increase in H atom concentration will cause the increase of hydrogen and 1,3-butadiyne yields by Reactions 48 and 49, respectively. The H atom responsible for the increase in the yields of major and minor hydrocarbons will be generated by the decomposition of formyl radical:

$$CHO \longrightarrow H + CO. \qquad (40)$$

Thus the concentration of H atom is increased by the presence of nitrogen oxide. H atom participated in all the secondary reactions to form ethylene, allene, propyne, and benzene such as[7]

$$H + C_2H_2 \longrightarrow C_2H_3 \xrightarrow{C_2H_2} C_2H_4,$$

$$
\begin{aligned}
&C_2H_3 + C_2H_2 \longrightarrow C_4H_5 \xrightarrow{C_2H_2} C_6H_7,\\
&C_6H_7 \longrightarrow C_3H_3 \xrightarrow{C_2H_2} C_3H_4,\\
&\qquad \longrightarrow C_6H_6.
\end{aligned}
$$

As can be seen from Fig. 9, the yields are hardly dependent on the amounts of nitrogen oxide added. At lower temperatures the yields of the above products are hardly increased by the addition of nitrogen oxide. The steady-state concentration of H atom in the absence of nitrogen oxide will be great enough relative to its increase by the addition of nitrogen oxide. With increase in temperature the H atom concentration increases gradually. The H atom, however, is converted into larger radicals by the subsequent reactions with acetylene. Thus the effect of the increase in the H atom concentration is averaged over the relevant radicals, the influence of the amounts of added nitrogen oxide being small.

The reactions mentioned above are too simple to give explicit formulas of major and minor hydrocarbons generation in the presence of nitrogen oxides. However, the main feature of the inhibited pyrolysis of acetylene can be interpreted by the present mechanism.

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