Thermal Decomposition of Acetaldehyde in the Presence of Hydrogen Sulfide. II. Effects of Chain-inhibitors

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In the foregoing paper[1], the present authors reported on the kinetics of the thermal decomposition of acetaldehyde in the presence of hydrogen sulfide and suggested that a part of the reaction involves a radical-chain mechanism, while the remaining part is probably molecular in character. Such an interpretation is based upon experiments in which the effects of various chain-inhibitors on the rate of decomposition were investigated. This paper reports on the results of these experiments. Propylene, isobutylene and nitric oxide were used as inhibitors.

Experimental

The preparation and purification of acetaldehyde and hydrogen sulfide were described in the foregoing paper[1]. Propylene was prepared by dehydration of isopropyl alcohol by pyrophosphoric acid supported on granular pumice at 250°C. Isobutylene was prepared from *tert*-butyl alcohol by a similar method. Nitric oxide was produced by the reaction of a concentrated sodium nitrite solution with a hydrochloric acid solution of ferrous chloride, decarbonated by a potassium hydroxide solution and dried by concentrated sulfuric acid and phosphorus

1) N. Imai, Y. Yoshida and O. Toyama, This Bulletin, 35, 752 (1962).

pentoxide. All of these gases were prepared in evacuated vessels and were purified by repeated bulb-to-bulb distillations. The apparatus and procedure were the same as those described in the foregoing paper[1].

Results and Discussion

As has been described in the foregoing paper, when acetaldehyde is decomposed thermally in the presence of hydrogen sulfide, the amount of acetaldehyde consumed is directly indicated by the increase in the total pressure. According to Smith and Hinshelwood[2], the pressure of acetaldehyde thermally decomposed in the presence of propylene also corresponds to the total pressure increase. It was confirmed in this work that such a correspondence between the amount of acetaldehyde decomposed and the total pressure change is retained even in the presence of both hydrogen sulfide and an inhibitor. Accordingly, the rate of decomposition was mostly calculated from the increase in the total pressure, as was the case in the absence of inhibitors.

Figure 1 shows the dependence of the rate of decomposition on the pressure of inhibitors, propylene and isobutylene, at constant pressures of acetaldehyde and hydrogen sulfide. It is seen that the rate decreases with the increasing pressure of the inhibitor until it attains a constant value, and that the rate of the fully inhibited reaction is almost the same for both inhibitors under otherwise constant conditions. Figure 1 shows, moreover, that the rate of fully inhibited reaction may be represented as

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_1[H_2S][CH_3CHO] \quad (I)$$

since the rate is proportional to the pressure of both hydrogen sulfide and acetaldehyde. Further evidence for Eq. I is given by Figs. 2 and 3, in which the rates of decomposition fully inhibited by propylene and by isobutylene are plotted.

It has been shown in the previous paper[1] that the rate of decomposition of acetaldehyde in the presence of hydrogen sulfide, but in the absence of any inhibitor, can be approximately represented by

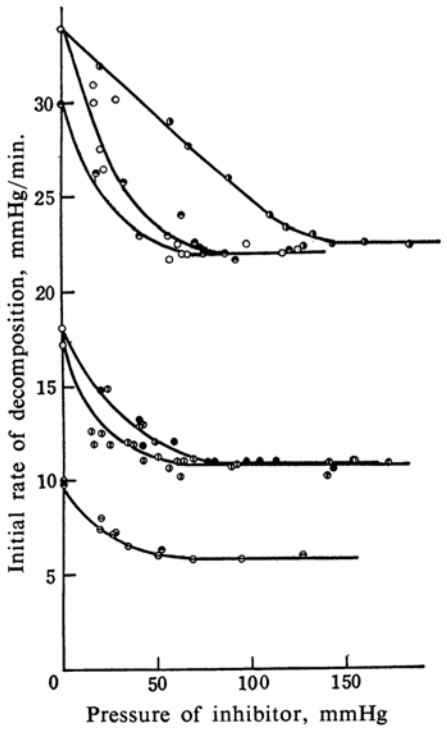

Fig. 1. Inhibition of acetaldehyde decomposition in the presence of hydrogen sulfide by propylene and isobutylene at 469°C.
Propylene: ● CH_3CHO 90 mmHg, H_2S 20 mmHg; ◑ CH_3CHO 50 mmHg, H_2S 40 mmHg; Isobutylene, ⊖ CH_3CHO 90 mmHg, H_2S 10 mmHg; ⊖ CH_3CHO 90 mmHg, H_2S 20 mmHg; ○ CH_3CHO 90 mmHg, H_2S 40 mmHg; ◓ CH_3CHO 180 mmHg, H_2S 20 mmHg

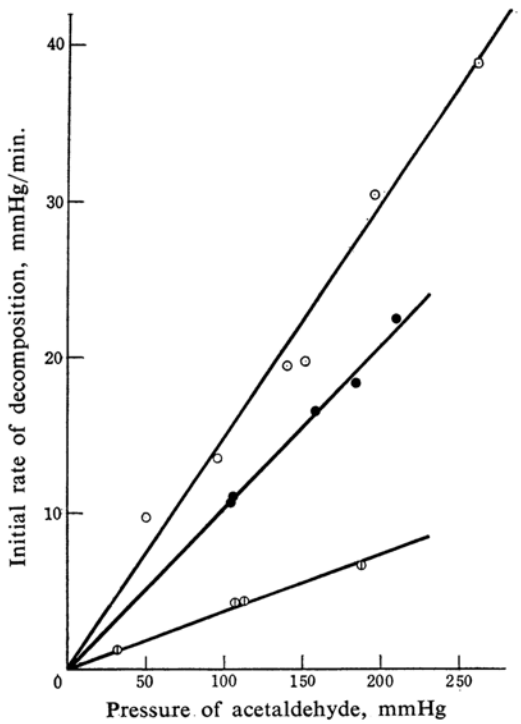

Fig. 2. Dependence on the pressure of acetaldehyde of the rate of isobutylene inhibited decomposition of acetaldehyde in the presence of hydrogen sulfide.
H_2S 20 mmHg, ⊖ 431°C; ● 469°C; ○ 494°C

2) J. R. E. Smith and C. N. Hinshelweed, *Proc. Roy. Soc.*, **A180**, 237 (1942).

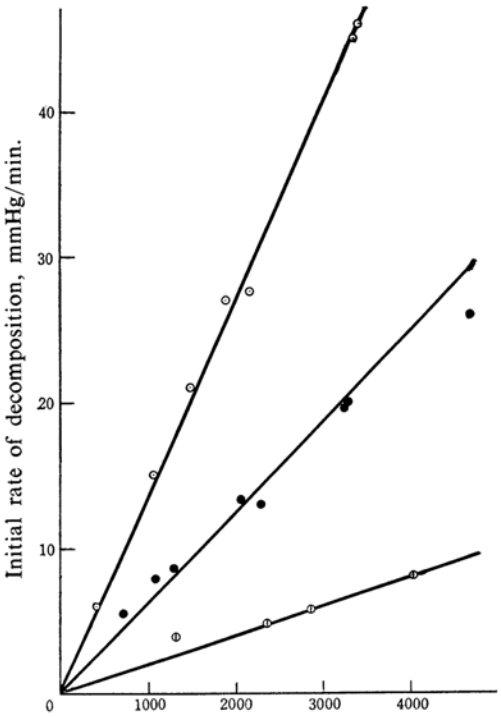

Fig. 3 Dependence of the rate of propylene-inhibited decomposition of acetaldehyde in the presence of hydrogen sulfide on the product of pressures of acetaldehyde and hydrogen sulfide.
◐ 431°C; ● 469°C; ○ 494°C

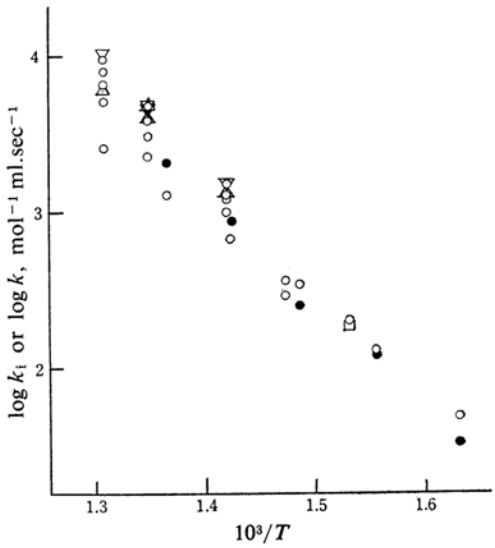

Fig. 4. Arrhenius plot of k_i and k.
▽ Propylene; △ Isobutylene; □ Nitric oxide; ○ k for the unpacked vessel; ● k for the packed vessel.

$$-d[CH_3CHO]/dt = k[H_2S][CH_3CHO] + k'[H_2S][CH_3CHO]^{1/2} \quad (II)$$

A comparison between Eqs. I and II shows that the former equation is of the same form as the first term of the latter. It is revealed on further examination that they are in fact identical. In Table I are listed the values of constant k_i in Eq. I obtained from the results given in Figs. 1—3; as seen in Fig. 4, these values are in agreement, within the limit of fluctuation, with those for k given in the preceding paper[1]. It may therefore be concluded that the addition of propylene or of isobutylene, in a sufficient quantity to bring about the maximum inhibition, eliminates the second term of Eq. II, leaving the first unaltered. Although there is much controversy[3] concerning the interpretation that the residual rate of pyrolysis of paraffins maximally inhibited by an inhibitor such as nitric oxide or propylene represents that of a non-chain, molecular decomposition, the results here obtained suggest that the second term of Eq. II represents a radical-chain decomposition, whereas the first term probably represents a hydrogen sulfide-catalyzed molecular decomposition which is not affected by chain-inhibitors.

TABLE I. VALUES OF k_i

Temp. °C	Inhibitor	Method	k_i mol^{-1} ml.sec^{-1}
380	Nitric oxide	Fig. 5	186
431	Propylene	Fig. 3	1530
	Isobutylene	Fig. 2	1320
469	Propylene	Fig. 1	4760
	Isobutylene	Fig. 1	4800
	Propylene	Fig. 3	4930
	Isobutylene	Fig. 2	4010
494	Propylene	Fig. 3	10700
	Isobutylene	Fig. 2	6000

Additional support for such an interpretation is provided by Fig. 5. The thermal decomposition of dimethyl ether in the presence of hydrogen sulfide, as was found in its absence, is explained entirely by a radical-chain mechanism[4]. When inhibited by nitric oxide, the rate of decomposition falls off to an almost negligible value, as is seen in the figure. The situation with acetaldehyde, on the other hand, is quite different. Here the residual rate of decomposition maximally inhibited by nitric oxide is still about half as large as that when uninhibited, and it yields a value of constant

3) A. Kuppermann and J. G. Larson, *J. Chem. Phys.*, **33**, 1264 (1960); B. W. Wojciechowski and K. J. Laidler, *Can. J. Chem.*, **38**, 1027 (1960); K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.*, **A259**, 257 (1960); **A260**, 103 (1961).
4) N. Imai and O. Toyama, This Bulletin, **34**, 328 (1961).

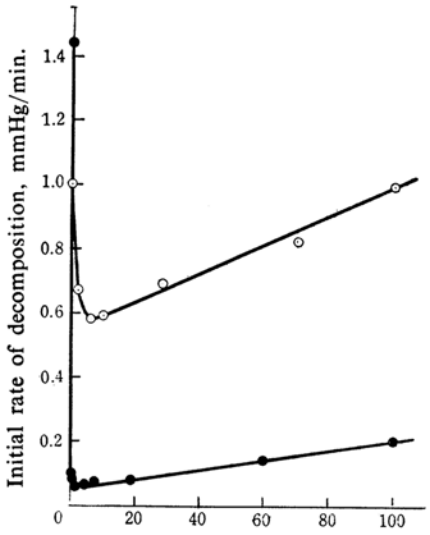

Fig. 5. Inhibition of decomposition of acetaldehyde and dimethyl ether in the presence of hydrogen sulfide by nitric oxide.
○ CH_3CHO 100 mmHg, H_2S 20 mmHg, 380°C; ● CH_3OCH_3 100 mmHg, H_2S 21 mmHg, 440°C

k_1 which is, again, in agreement with that of k as shown in Fig. 4[5].

As is seen in Fig. 5, the rate of decomposition of acetaldehyde as well as of dimethyl ether increases, after passing through a minimum, in proportion to the pressure of nitric oxide added. In view of the complete inhibition of the chain decomposition, as inferred above, these results suggest that nitric oxide catalyzes the molecular decomposition of these compounds[6]. For acetaldehyde in the absence of hydrogen sulfide, a similar behavior of nitric oxide has already been reported by Smith and Hinshelwood[2]. For paraffins, inhibitors such as propylene and isobutylene behave similarly[7]. In the latter case, however, there is serious doubt that the residual decomposition after being maximally inhibited is molecular in character[3].

Jack et al.[7] reported the relative efficiencies of propylene, isobutylene and nitric oxide as inhibitors to be 1 : 1.6 : 11 in the thermal decomposition of *n*-pentane at 560°C. Hinshelwood et al. have shown that nitric oxide is 5 to 100 times as effective as propylene for the inhibition of the decomposition of various organic compounds[2,8]. Figures 1 and 5 show that the results obtained in this work are similar. Rate constants are reported to be $10^{10.8}\exp(-7700/\boldsymbol{RT})$[9], $10^{10.9}\exp(-7300/\boldsymbol{RT})$[9] and $10^{11.1}\,\mathrm{mol^{-1}\,ml.\,sec^{-1}}$[10] for the reactions between methyl radical and propylene, isobutylene and nitric oxide respectively. Other values of 6.4 and 4.1 kcal. $\mathrm{mol^{-1}}$ are reported for the activation energies of the former two reactions respectively[11]. These values are at least qualitatively in agreement with the efficiencies of the three inhibitors.

Summary

The effect of propylene, isobutylene and nitric oxide as inhibitors on the thermal decomposition of acetaldehyde in the presence of hydrogen sulfide has been investigated over the temperature range of 380 to 494°C. Of the three inhibitors, which are all effective in reducing the rate of decomposition, isobutylene is slightly more efficient than propylene, and nitric oxide is far more efficient than the other two. With propylene and isobutylene, the rate of decomposition is reduced with the increasing amount of the inhibitor until a constant rate is reached, while with nitric oxide the rate passes through a minimum value and then increases again in proportion to the pressure of the inhibitor. The residual rate of the maximally inhibited decomposition is almost the same for the three inhibitors and is represented by $-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_1[H_2S]\,[CH_3\cdot CHO]$. A comparison of the above results with those of the decomposition in the absence of an inhibitor suggests that the residual decomposition remaining after being fully inhibited is a molecular process catalyzed by hydrogen sulfide.

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5) The value of k_1 in this case was obtained by extrapolation of the linear plot following the minimum in Fig. 5.
6) A further study of the catalytic effect exerted by nitric oxide on the residual decomposition of dimethyl ether after being maximally inhibited is now in progress in our laboratory.
7) J. Jack, F. J. Stubbs and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A224**, 283 (1954).
8) J. R. E. Smith and C. N. Hinshelwood, ibid., **A183**, 33 (1944); F. J. Stubbs and C. N. Hinshelwood, ibid., **A200**, 458 (1950).
9) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 169 (1951).
10) W. A. Bryce and K. U. Ingold, ibid., **23**, 1968 (1955).
11) A. D. Stepukhovich and E. S. Shver, *Zhur. Fiz. Khim.*, **27**, 1013 (1953).