Hydrogen Abstraction from Hydrogen Sulfide Molecules by Methyl Radicals

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A study of the hydrogen sulfide catalyzed thermal decomposition of acetaldehyde carried out in this laboratory suggested that the catalysis is at least in part ascribed to hydrosulfide radicals produced by the reaction of methyl radicals with hydrogen sulfide molecules. It seemed then desirable to investigate this hydrogen abstraction reaction quantitatively, for only limited information was available on this reaction.

The technique used in this work is one of the competitive methods which have frequently been applied to study reactions of free radicals: acetone vapor has been photolyzed in the presence of varied amounts of hydrogen sulfide; the analysis of the products has yielded the ratio of the rate of the abstraction reaction in question to that of the recombination reaction of methyl radicals; the rate of the former reaction can then be estimated since that of the latter has already been the subject of a number of extensive investigations.

Experimental

Materials.—Acetone used in this experiment was supplied commercially and purified by bulb-to-bulb distillation. Hydrogen sulfide was prepared by dropping water on aluminium sulfide in a vacuum system, dried by passing through a trap at −78°C and purified by bulb-to-bulb distillation. Cupric oxide and cupric sulfate used in analyses were commercial samples.

Apparatus. — Photolysis was carried out in a cylindrical quarz vessel of about 110 cc. capacity placed in an electric furnace with a glass window which cuts off the light of a wave length shorter than 2800 Å. Therefore, no light was absorbed by hydrogen sulfide. The reaction vessel was connected to a mercury manometer, to an analytical system, and to a capillary tube of small volume, which had a mercury manometer and was used to measure a small quantity of hydrogen sulfide to be admitted to the vessel. The full light from a medium-pressure mercury arc was used in the present experiment. In order to increase light intensity it was placed at a focus of a half spheroidal mirror and at the other focus the center of the vessel was placed. Light intensity was kept constant by using a voltage stabilizer. The vessel, manometer, storage bulbs and the analytical system were attached to a conventional vacuum line.

Procedure.—A small measured quantity of hydrogen sulfide was admitted to the reaction vessel. Acetone vapor with a desired pressure was then added. After a few minutes to allow the gases to mix thoroughly and to come to a desired temperature, light was admitted into the vessel and irradiation was continued for a desired time.

Analysis.—After the photolysis, using a Toepler gauge, the reactants and products were passed through a trap at −78°C where the unreacted acetone and low boiling point products were condensed. The uncondensable fraction at −78°C was passed through a trap at −196°C and the quantity of uncondensable fraction at −196°C was measured by Toepler gauge. This fraction contained methane and carbon monoxide and was passed over cupric oxide at 250°C where carbon monoxide was oxidized to carbon dioxide and hydrogen, if any, to water. By the Toepler gauge these gases were passed through a trap at −78°C where water, if any, was condensed, and through another one at −196°C where carbon dioxide was condensed. The uncondensable fraction contained only methane, and its quantity was measured by the Toepler gauge. The condensed carbon dioxide was vaporized at room temperature and its quantity was measured by a McLeod gauge connected with the trap. The quantity of product uncondensable at −196°C was always equal to the sum of quantities of methane and carbon monoxide analyzed within an error of 1%. That no water was found in all the runs showed that no hydrogen was formed in the photolysis. The fraction uncondensable at −78°C and condensable at −196°C contained the remaining hydrogen sulfide, ethane and other products. This fraction was vaporized and led to a trap at −196°C through another one at about −160°C. The uncondensable fraction at −160°C was vaporized and measured by the McLeod gauge. This fraction should have contained only hydrogen sulfide and ethane. Hydrogen sulfide was removed by contact with dry cupric sulfate. Thus the quantities of ethane and hydrogen sulfide were determined separately.

Results and Discussion

A series of preliminary experiments with varied times of irradiation under otherwise constant conditions revealed that all the rates of formation of carbon monoxide, methane and ethane remain nearly constant at least during the initial stage of the photolysis up to about 0.2% conversion, which justifies the computation of initial rates of formation of these products from the analytical results at such low

TABLE I. THE EFFECT OF HYDROGEN SULFIDE ON THE PHOTOLYSIS OF ACETONE

Temp. °C	Initial concentration mol. cc^{-1}		Time sec.	Rate of formation mol. cc^{-1} sec^{-1}			$R_{CH_4}/R_{C_2H_6}{}^{1/2}$ $\times 10^6$
	[Acetone]$_0$ $\times 10^6$	[H$_2$S]$_0$ $\times 10^9$		R_{CO} $\times 10^{12}$	R_{CH_4} $\times 10^{12}$	$R_{C_2H_6}$ $\times 10^{12}$	
50	3.87	0	3000	6.01	0.968	6.52	0.38
	3.92	0	2000	6.00	1.05	6.45	0.41
	3.85	3.02	200	9.2	6.5	5.25	2.84
	3.90	4.22	300	6.73	8.17	3.81	4.27
	3.89	4.9	300	9.1	9.0	3.77	4.64
	3.89	5.3	300	7.23	9.1	3.30	5.00
	3.86	8.2	400	5.74	11.1	2.00	7.88
	3.89	9.9	500	5.40	12.5	1.80	9.33
90	3.92	0	3000	20.6	3.28	18.6	0.752
	3.87	0	1000	25.4	3.77	21.0	0.823
	3.90	1.57	100	24.3	12.2	15.2	3.13
	3.87	2.48	100	24.8	15.9	13.7	4.30
	3.90	3.65	100	25.0	18.3	10.7	5.6
	3.90	5.0	200	22.0	21.7	7.75	7.8
	3.87	6.3	200	22.0	24.2	7.62	8.8
	3.89	9.5	200	22.5	27.3	5.12	12.1
	6.94	0	2000	29.3	6.80	22.5	1.43
	6.92	2.83	100	39.3	22.6	21.5	1.89
	6.93	4.2	200	37.5	28.2	18.4	6.57
	6.91	6.0	100	37.0	34.9	13.5	9.51
	6.90	9.1	200	30.6	37.3	6.64	14.4
	6.88	11.3	200	28.0	38.8	5.57	16.5
140	3.88	0	3000	39.3	15.0	29.0	2.79
	3.88	0	3600	41.8	15.1	28.0	2.85
	3.88	1.70	100	35.2	25.4	14.5	6.06
	3.89	3.80	100	3[illegible].9	31.6	8.60	10.8
	3.87	4.75	100	31.0	32.0	6.60	12.4
	3.88	6.5	200	30.0	35.4	4.62	16.5
	3.88	8.5	200	29.0	36.8	3.33	20.2
200	3.85	0	1000	41.2	34.2	11.0	10.3
	3.39	0	2000	22.3	22.0	5.20	9.4

conversions[1]. In Table I are listed the initial rates of formation of these products thus determined in several series of experiments. Within a series only the initial concentration of hydrogen sulfide was varied to determine the dependence of the rate on its concentration. The intensity of light was kept nearly constant throughout all the runs. As the concentration of hydrogen sulfide was increased, the rate of formation of ethane was decreased as seen in the table. On the other hand, use of too much hydrogen sulfide made its removal by dry cupric sulfate in analysis incomplete so that the rate of ethane formation was then liable to be overestimated. This situation limited the concentration range for hydrogen sulfide to those given in Table I.

It has been established[2-5] that during the photolysis of acetone, metane, ethane and carbon monoxide are produced almost entirely by the following reactions:

$$CH_3COCH_3 + h\nu = CH_3CO + CH_3 \quad (1)$$

$$CH_3CO = CH_3 + CO \quad (2)$$

$$CH_3 + CH_3 = C_2H_6 \quad (3)$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2 \quad (4)$$

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1) It was found in the present work that the hydrogen sulfide initially added is consumed as the photolysis is continued. The ultimate fate of the hydrogen sulfide will be dealt with in a later paper.

2) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

3) A. F. Trotman-Dickenson and E. W. R. Steasie, ibid., **18**, 1097 (1950).

4) R. Gomer and G. B. Kistiakowsky, ibid., **19**, 851 (1951).

5) M. T. Jaquiss, J. S. Roberts and M. Szwarc, *J. Am. Chem. Soc.*, **74**, 6005 (1952).

Reactions 3 and 4 lead to the following equation

$$R_{CH_4}/R_{C_2H_6}{}^{1/2} = (k_4/k_3{}^{1/2})\,[CH_3COCH_3] \qquad (I)$$

which is in agreement with experimental results. In the presence of hydrogen sulfide, the reaction

$$CH_3 + H_2S = CH_4 + HS \qquad (5)$$

may occur[6] and reactions 3, 4 and 5 taken together now yield

$$R_{CH_4}/R_{C_2H_6}{}^{1/2} = (k_4/k_3{}^{1/2})\,[CH_3COCH_3] + (k_5/k_3{}^{1/2})\,[H_2S] \qquad (II)$$

When the concentration of acetone is kept constant, the plot of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ vs. $[H_2S]$ should give a straight line, and its intercept should be equal to the value of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ in the absence of hydrogen sulfide. Fig. 1 shows such plots of the results given in Table I and it is seen that the above requirements are in fact satisfied. That the slope of the straight line is not affected by a two-fold increase in the acetone concentration at 90°C may be taken as additional evidence for the validity of Eq. II. From the slopes of these straight lines, values of $k_5/k_3{}^{1/2}$ at various temperatures were determined and are shown in Table II together with those of $k_4/k_3{}^{1/2}$ obtained in the absence of hydrogen sulfide.

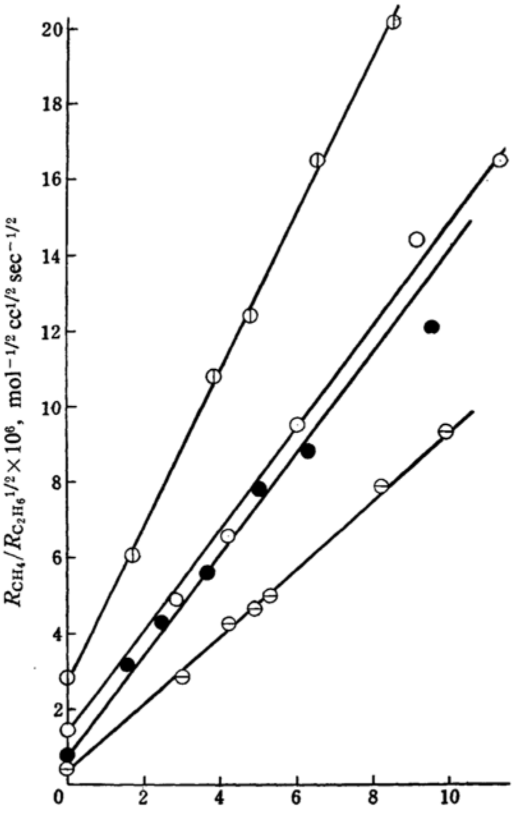

Fig. 1. Dependence of the ratio $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ on the concentration of hydrogen sulfide.
⊖, $[\text{Acetone}]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 50°C;
●, $[\text{Acetone}]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 90°C;
○, $[\text{Acetone}]_0 = 6.9 \times 10^{-6}$ mol. cc^{-1}, 90°C;
⦶, $[\text{Acetone}]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 140°C.

TABLE II. VALUES OF $k_5/k_3{}^{1/2}$ AND $k_4/k_3{}^{1/2}$

Temp. °C	$k_5/k_3{}^{1/2}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$	$k_4/k_3{}^{1/2}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$
50	880	0.102
90	1350	0.210
140	2080	0.727
200	—	2.71

The Arrhenius plot of $k_4/k_3{}^{1/2}$ shows a curvature at temperatures below 100°C as is well known. According to Ausloos and Steacie[7] this falling off in the apparent activation energy at low temperatures presumably arises from a reaction between methyl radicals and adsorbed acetone molecules on the wall and a disproportionation reaction between methyl radicals and acetyl radicals. The excessive value of $k_4/k_3{}^{1/2}$ in question, however, caused no more than 3% error in the value of $k_5/k_3{}^{1/2}$ even at 50°C. The values of $k_4/k_3{}^{1/2}$ at 140° and 200°C are in satisfactory agreement with those previously reported[2-5].

In contrast, the Arrhenius plot of $k_5/k_3{}^{1/2}$ yielded a good straight line from which $E_5 - 1/2E_3 = 2.6$ kcal. mol^{-1} and $A_5/A_3{}^{1/2} = 10^{4.675}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$ are obtained, where E denotes the activation energy and A the pre-exponential factor. Accepting the values $E_3 = 0$ and $A_3 = 10^{13.38}$ mol^{-1} cc. sec^{-1} as recommended by Shepp[8] we find

$$k_5 = 10^{11.4} \exp(-2{,}600/\boldsymbol{R}T) \ \text{mol}^{-1}\,\text{cc. sec}^{-1}$$

The value of $A_5 = 10^{11.4}$ mol^{-1} cc. sec^{-1} seems to be reasonable, since most A factors for hydrogen abstraction reactions by methyl radicals are of the order of 10^{11} mol^{-1} cc. sec^{-1}.

On the other hand, the value of $E_5 = 2.6$ kcal. mol^{-1} might be regarded unexpectedly low. Birrell, Smith, Trotman-Dickenson and Wilkie[9] have reported that the apparent order of reactivities of thiols towards methyl radical are given by

$$Bu^tSH > Pr^iSH > EtSH > MeSH > H_2S$$

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[6] Subsequent reactions of hydrosulfide radicals formed by reaction 5 are under investigation. There is, however, little indication that these reactions affect the importance of reaction 3 in forming ethane and that any other important source of methane besides reactions 4 and 5 must be considerd.

[7] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).

[8] A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

[9] R. N. Birrell, R. F. Smith, A. F. Trotman-Dickenson and H. Wilkie, *J. Chem. Soc.*, 1957, 2807.

According to Kerr and Trotman-Dickenson[10], the rate constants of hydrogen abstraction from thiols by methyl radical at 30°C are

MeSH 1.8, EtSH 3.5, $\mathrm{Pr^iSH}$ 4.1, $\mathrm{Bu^tSH}$ 5.9

in $10^{-7}\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$. From these values they estimated the activation energies between 4.9 and 5.6 kcal. $\mathrm{mol^{-1}}$, assuming $A=10^{11.3}\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$. If the estimations given by these two studies are accepted altogether and the same value of A is assumed for reaction 5, E_5 can not be lower than 5.6 kcal. $\mathrm{mol^{-1}}$, while a much lower value of 2.6 kcal. $\mathrm{mol^{-1}}$ has actually been found in this work. Presumably, there is some error in the order of reactivity estimated by Birrell et al. on the basis of qualitative considerations; although this order of reactivity for a series of thiols from methane thiol to isobutane thiol is in agreement with that of rate constrants found by Kerr and Trotman-Dickenson, and hence may be taken as established, there seems to be no convincing evidence for the least reactivity of hydrogen sulfide[11]. The expression for k_5 obtained in the present work gives $k_5=3.3\times10^9\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$ at 30°C, a value far greater than Kerr and Trotman-Dickenson's rate constants for thiols cited above.

The results given in Table I show that the rate of formation of carbon monoxide, on the whole, increases with temperature in agreement with the previous observation[12-14] on the quantum yield of carbon monoxide. There is some indication in the table at low temperatures that the addition of a small quantity of hydrogen sulfide increases the rate of formation of carbon monoxide, while greater concentration of hydrogen sulfide lowers the rate though the effect is not great at high temperatures. The probable explanation for these findings seems to be given by the promotion of the primary decomposition by hydrogen sulfide and the reaction of acetyl radical with hydrogen sulfide, though anything conclusive cannot yet be drawn at present on these problems.

Summary

Acetone has been photolyzed in the presence of the varied amounts of hydrogen sulfide in the temperature range from 50° to 140°C. From the analysis of the products at low conversions the initial rates of formation of carbon monoxide, methane and ethane have been determined, which, combined with the mechanism of acetone photolysis already established, give the values of $k_5/k_3{}^{1/2}$, where k_5 and k_3 are respectively the rate constants for the reactions $CH_3+H_2S=CH_4+HS$ and $CH_3+CH_3=C_2H_6$. Accepting $k_3=10^{13.38}\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$ with zero activation energy as recommended by Shepp, the rate constant of the abstraction reaction is represented by $k_5=10^{11.4}\exp(-2.6\ \mathrm{kcal.\,mol^{-1}}/\boldsymbol{R}T)\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$.

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[10] J. A. Kerr and A. F. Trotman-Dickenson, ibid., 1957, 3322.

[11] Birrell et al. themselves described that their interpretation of the results with hydrogen sulfide was somewhat uncertain.

[12] R. Spence and W. Wild, *J. Chem. Soc.*, 1937, 352.

[13] D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 62, 2052 (1940).

[14] H. W. Anderson and G. K.Rollefson, ibid., 63, 816 (1941).