

215°, 223–226°, 222–224°. A sample of luteolin tetraacetate was synthesized according to the method of Kostanecki, Rozycki and Tambor,⁸ starting with methyl veratrate and trimethoxyacetophenone. The synthetic material melted at 221–222° and a mixture of this and that from the natural source melted at 219–221°. In a repetition of the isolation from the florets and bracts there was obtained a product melting at 220–222°. The natural and synthetic samples gave identical red-orange colors when to their solutions in alcohol were added a fragment of magnesium and a drop of concentrated hydrochloric acid, and both samples dissolved in hot alcoholic sodium hydroxide to form yellow solutions. Unfortunately too little of the material from the natural source was obtained for satisfactory analytical figures. Each of the two samples described was analyzed.

Anal. Calcd. for $C_{27}H_{18}O_{10}$: C, 60.78; H, 4.00. Found: C, 61.74, 60.15, 60.29; H, 4.27, 4.04, 3.80.

It is felt, however, that the information from the melting point and color-test observations, coupled with the approximate agreement in the analyses is sufficient to establish the identity of the compound isolated.

From the oily mother liquor from which the crude luteolin separated was obtained a crystalline mixture of acetates; m. p. 130–190°. It formed a deep red solution in hot alcoholic alkali. Too little of it was obtained to permit of its separation into its components.

Isoquercitrin.—The alcohol extract of the ether-extracted meal (disk-florets and bracts) was diluted with water and concentrated to remove most of the alcohol. Saturated lead acetate was added in small portions and the brown precipitates which first appeared were discarded. The bright orange-yellow precipitate which then formed was removed, suspended in hot water and decomposed with

hydrogen sulfide. The filtered solution was saturated with salt and extracted with ethyl acetate. Removal of the ethyl acetate left a yellow gum which on standing in alcohol–water solution deposited 60 mg. of a yellow powder. This crystallized from dilute alcohol as lemon-yellow needles; m. p. 217–219° after shrinking at about 115° (loss of water of hydration). It dissolved in alkali to a deep yellow solution, gave a deep olive-green color with aqueous-alcoholic ferric chloride and a rose-red solution when reduced in alcoholic solution with magnesium-hydrochloric acid. These observations are in agreement with those recorded for isoquercitrin (quercetin-3-glucoside); m. p. reported as 217–219°, 218–220°, 219°. ¹¹

Hydrolysis of 24.0 mg. of the glycoside with 6 ml. of 1 *N* sulfuric acid yielded 14.1 mg. of quercetin; calcd. for isoquercitrin, 14.4 mg. The product of the hydrolysis was converted into its acetate, m. p. 192–193°; no depression on mixing with an authentic sample, m. p. 193–194°, of quercetin pentaacetate.

Anal. Calcd. for quercetin pentaacetate, $C_{26}H_{20}O_{12}$: C, 58.58; H, 3.94. Found: C, 58.66; H, 3.99.

Summary

1. The flowers of *Cosmos sulphureus* ("Orange Flare") contain coreopsin (rays), luteolin and a quercetin glycoside which is probably isoquercitrin (disk-florets and involucre bracts).

2. Coreopsin has been found to be a butein glycoside. The nature and position of the sugar residue are as yet undetermined.

(9) Perkin, *J. Chem. Soc.*, **95**, 2190 (1909).

(10) Sando and Bartlett, *J. Biol. Chem.*, **54**, 640 (1922).

(11) Viehover, Chernoff and Johns, *J. Agr. Research*, **13**, 348 (1918).

(6) Perkin, *J. Chem. Soc.*, **69**, 206 (1896).

(7) Herzig, *Ber.*, **29**, 1013 (1896).

(8) Kostanecki, Rozycki and Tambor, *ibid.*, **33**, 3416 (1900).

LOS ANGELES, CALIFORNIA

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The Catalysis of the Thermal Decomposition of Acetaldehyde by Hydrogen Sulfide

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In some previous work it has been shown that the acceleration of the rate of the thermal decomposition of acetaldehyde when iodine is added is due to a series of reactions in which the iodine reacts with the aldehyde and then is regenerated by reactions between the products of the first reaction.¹ In this paper we are presenting the results of some investigations of the nature of the action of hydrogen sulfide which has also been reported to accelerate the decomposition of acetaldehyde.²

Fromherz reported that the rate of the decom-

position in the presence of hydrogen sulfide is dependent only on the pressure of the catalyst. In accordance with this statement the rate was constant throughout a considerable portion of any given run and the ratio of the time required for three-fourths completion to that required for half completion was approximately 1.5 as it should be if the rate were independent of the aldehyde pressure. On the other hand, if we utilize this linear character of the pressure–time curves to calculate the initial rates, we find continuous variation of the rate constants calculated on the assumption of independence of the aldehyde according to the

(1) Faulk and Rollefson, *This Journal*, **59**, 625 (1937).

(2) Fromherz, *Z. physik. Chem.*, **B28**, 301 (1934).

law $-d(\text{CH}_3\text{CHO})/dt = k'(\text{H}_2\text{S})$. The results for a series of aldehyde pressures are shown in Table I along with the times given by Fromherz for a pressure change one-half and three-fourths of the final value.

TABLE I

Temperature 510°, H ₂ S 20 mm.				
CH ₃ CHO mm. initial	$t_{1/2}$, min.	$t_{3/4}$, min.	$t_{3/4}/t_{1/2}$	k' , min. ⁻¹
58	1.44	2.36	1.64	10.05
106.5	2.10	3.35	1.59	12.65
129	2.37	3.73	1.58	13.60
149	2.49	3.94	1.58	14.95
182.5	2.60	4.12	1.58	17.55
273	2.73	4.50	1.64	25.00
383	2.77	4.61	1.66	34.60

If the reaction were truly of the zero order with respect to the acetaldehyde the value in the fourth column should be 1.5 and the value in the fifth column should be constant. It is apparent that while the values of the ratios $t_{3/4}/t_{1/2}$ are approximately constant the value is too large and k' shows a marked trend with the initial pressure of the aldehyde. The experiments reported in this paper were designed to determine the true rate law for this reaction and to test several hypotheses concerning the mechanism of the catalysis.

Apparatus, Methods, and Materials.—The apparatus was of the type usually employed in the study of gaseous reactions in which the progress of the reaction can be followed by pressure measurements. The volume of the system was kept constant and the pressure measured by means of a click gage with the aid of a sulfuric acid manometer for the low pressures and a mercury manometer for the higher pressures. The reaction vessel was placed in a cylindrical electrical furnace, wired concentrically, and equipped with end heaters to eliminate temperature gradients. The furnace temperature was kept constant to 1° by manually controlled rheostats. Temperatures were measured with a chromel-alumel thermocouple which had been calibrated at the melting points of lead, tin and zinc. The thermocouple was placed in a well which extended to the center of the reaction vessel.

On account of the extreme sensitivity of the reaction to traces of air, all operations were carried out in a system which could be evacuated to a pressure of 10^{-6} mm. before starting an experiment. The sulfuric acid manometer was always separated from the reaction vessel by the click gage.

Experiments were performed with two Pyrex and one quartz reaction vessel. One of the Pyrex vessels was packed with glass tubing to increase the surface/volume ratio in some of the experiments. The surface/volume ratios were approximately unity in the unpacked vessels and 12 in the packed one. The volumes of the unpacked vessels ranged from 219 cc. to 379 cc. with a surface/volume ratio of ca. unity and the packed vessel had a free volume of 180 cc. with a surface/volume ratio of 12.

Acetaldehyde was purified by three different procedures. The only sample which was free from the effects which were found to be due to the presence of small amounts of air was one for which the entire preparation was carried out in a system which had been thoroughly evacuated. Merck paraldehyde which had been washed with sodium bicarbonate, dried over calcium chloride, and fractionated was depolymerized with a trace of concentrated sulfuric acid. The middle fraction was refluxed under vacuum, put in contact with recrystallized hydroquinone and calcium sulfate for twenty-four hours and fractionated, the middle fraction being saved for use. This sample was stored at 0° behind a mercury cutoff and small amounts distilled as needed into a second reservoir where it was given an additional degassing at -78° before using.

Some of the experiments were performed with hydrogen sulfide which had been obtained from the Ohio Chemical Company and had been degassed by repeated evacuations at -180° . The final results were obtained with a sample made from electrolytic hydrogen and sulfur.

Electrolytic hydrogen, free from oxygen, was supplied by Professor Giauque of this Laboratory.

The sulfur used was a sample prepared by Eastman and McGavock for heat capacity investigations.³

Carbonyl sulfide was prepared from ammonium thiocyanate and sulfuric acid.⁴

Nitric oxide which had been prepared by the method of Johnston and Giauque⁵ was supplied by Dr. K. Atwood.

Eastman Kodak Company methyl mercaptan and Kahlbaum dimethyl sulfide were distilled and degassed in the vacuum system.

Distilled water was degassed thoroughly by boiling and distilling off the first half in the vacuum line.

The procedure followed in making a typical run and analysis was: The reaction vessel was first flushed with acetaldehyde, evacuated, and then hydrogen sulfide introduced and the pressure measured. Next the acetaldehyde was admitted and an electric clock started simultaneously. Pressure readings were taken at regular intervals, usually of one-half minute, during the initial stages of the reaction. The initial total pressure was determined by extrapolating the pressure-time curve to zero time.

When the pressure change indicated that the reaction had proceeded as far as was desired for that experiment the gases were drawn from the reaction vessel by means of a Toepler pump. Two spiral traps immersed in liquid air inserted between the vessel and the pump served to freeze out all of the condensable gases. The non-condensable gases were transferred to a gas buret and samples were analyzed by the micromethods which have been described by Blacet, Leighton, MacDonald and others.⁶ The condensable gases were analyzed for hydrogen sulfide by treating them with a solution of lead nitrate and titrating the liberated acid with a solution of 0.01 *N* sodium hydroxide. Blank experiments showed that acetaldehyde and lead sulfide did not interfere with this analysis.

(3) Eastman and McGavock, *THIS JOURNAL*, **59**, 145 (1937).

(4) Kemp and Giauque, *ibid.*, **59**, 79 (1937).

(5) Johnston and Giauque, *ibid.*, **51**, 3194 (1929).

(6) (a) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 766 (1931); (b) Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933); (c) Blacet and MacDonald, *ibid.*, **6**, 334 (1934); (d) Blacet and Volman, *ibid.*, **9**, 44 (1937).

Results and Discussion.—Preliminary experiments showed that consistent results could not be obtained unless the reactants were carefully purified especially so as to eliminate oxygen. This observation is in agreement with that of Letort⁷ who found that the thermal decomposition of acetaldehyde is accelerated by small amounts of oxygen. Furthermore with reactants which had not been carefully purified the reaction was found to be partially heterogeneous but it was immaterial whether the surface was quartz or Pyrex glass. With carefully purified reactants the reaction was found to be homogeneous as is shown by the data in Table II. The packed vessel had a surface/volume ratio twelve times that of the unpacked one. The remainder of this paper is concerned with this homogeneous reaction.

TABLE II

COMPARISON OF RATES IN QUARTZ AND PACKED PYREX REACTION VESSELS AT 713°K.

Initial pressure, cm. of mercury	Initial rate/(H ₂ S)	Reaction vessel	
H ₂ S	CH ₃ CHO	cm./min.	
3.68	18.79	0.324	Packed Pyrex
4.04	19.77	.296	Quartz
4.04	18.62	.268	Packed Pyrex
4.03	19.19	.265	Quartz
2.12	17.36	.821	Packed Pyrex
1.98	20.72	.824	Quartz

Analysis of the reaction mixture at various degrees of completion showed that the only products present in appreciable amounts were methane and carbon monoxide. Within the limits of accuracy of the methods used, the hydrogen sulfide was present in its original form throughout the course of the reaction. Some of the analytical results are shown in Table III. It follows from these observations that the pressure change at any time is a measure of the extent of the reaction.

Some typical pressure time curves are shown in Fig. 1. It is apparent that the curves are practically linear for the first half of the reaction or even more at high pressures but at low initial pressures and toward the end of the reaction the deviations from linearity are appreciable. These observations are in accord with those of Fromherz to the effect that over a wide range in any given run the rate is independent of the acetaldehyde pressure. However, the markedly different slopes of the three curves shown in Fig. 1 show that the initial rates are dependent on the aldehyde pressure. From a large number of initial rate measurements,

(7) Letort, *J. Phys. Chem.*, **34**, 355 (1937).

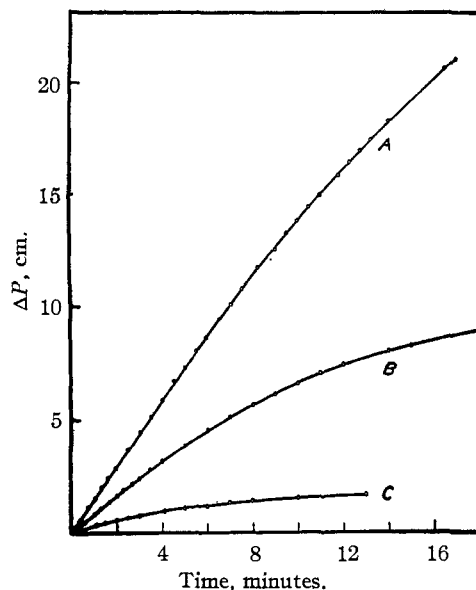


Fig. 1.—Pressure-time curves of the sensitized decomposition of acetaldehyde: 713°K.; H₂S, 4.00 cm.; CH₃CHO: A—31.70 cm., B—10.94 cm., C—2.04 cm.

the details of which are listed in Table V, it was found that the initial rates could be expressed by

$$-d(\text{CH}_3\text{CHO})/dt = k_1(\text{H}_2\text{S})(\text{CH}_3\text{CHO}) + k_2(\text{H}_2\text{S})(\text{CH}_3\text{CHO})/(1 + k_3(\text{CH}_3\text{CHO}))$$

in which the formulas in parentheses represent the initial pressures of aldehyde and hydrogen sulfide and the constants have the following values at 713°K.

$$k_1 = 0.0081 \text{ cm.}^{-1}\text{min.}^{-1} = 1.82 \times 10^{-6} \text{ mole}^{-1}\text{liter min.}^{-1}$$

$$k_2 = 0.0833 \text{ cm.}^{-1}\text{min.}^{-1} = 1.88 \times 10^{-5} \text{ mole}^{-1}\text{liter min.}^{-1}$$

$$k_3 = 0.667 \text{ cm.}^{-1} = 1.50 \times 10^{-4} \text{ mole}^{-1}\text{liter}$$

It was found that the decomposition products, methane and carbon monoxide do not affect the rate. Furthermore, the addition of a fresh charge of aldehyde at the end of a run gave the same rate as if the aldehyde and hydrogen sulfide had been mixed directly, thus showing that the catalytic activity of the sulfide was not reduced by use. In Table III the last column gives the rate as calculated by the above equation. The rate during any given run could be fitted by a similar

TABLE III
ANALYTICAL RESULTS

Initial pressure, cm. of Hg.	% completion	Non-condensable gases, %	H ₂ S found, %	
H ₂ S	CH ₃ CHO	CH ₄	CO	
1.94	9.61	50.2	49.8	97.2
1.95	13.40	50.3	49.4	98.7
23.99	5.00	49.7	50.3	..
55.95	0.90	49.3	49.2	..
2.58	7.20	51.0	49.0	98.7
1.94	6.13	49.9	49.8	99.4

equation but the value of k_2 would have to be much larger relative to k_1 .

The effect of temperature on the rate is shown by the data in Table IV. In a simple reaction a corresponding change with temperature would be found if the activation energy were 36 kcal.

TABLE IV
RATES AT DIFFERENT TEMPERATURES

Temp., °K.	Initial pressure (cm. of mercury)		Initial rate cm./min.
	H ₂ S	CH ₃ CHO	
713	2.00	20.00	0.556
728	2.05	20.67	1.07
744	1.96	20.72	1.63
760	1.98	20.48	2.65
772	2.00	19.98	4.13
776	2.03	21.15	4.57
786.5	2.00	21.10	5.98

Since the analyses failed to give any indication of the nature of the intermediary steps in the catalysis a number of experiments were performed with various substances which might be present in the reaction mixture in very minute amounts or which on the basis of structural similarity might be expected to have an effect similar to that of hydrogen sulfide. The results obtained, all at 713° K., were as follows:

Sulfur causes the aldehyde to decompose approximately five times as fast as in the presence of the corresponding amount of hydrogen sulfide. Within a few minutes the sulfur is converted into hydrogen sulfide, and the rate of decomposition becomes that determined by the latter substance.

If it is assumed that the hydrogen sulfide catalysis involves the hydrogen sulfide-sulfur equilibrium the addition of hydrogen to the reaction mixture should decrease the rate of the reaction. Actually it was found that the addition of 30.91 cm. of hydrogen decreased the rate only 14%. At intermediate pressures the effect was proportional to this value. The dependence of the rate on the aldehyde and hydrogen sulfide pressures was not altered by the addition of hydrogen. This result in itself tends to exclude the hypothesis of the sulfide-sulfur equilibrium. Additional ground for excluding that idea is supplied by the fact that the observed rate was 28 times that calculated from the data in the literature on the equilibrium and our observations on the effect of sulfur.

The effect of carbonyl sulfide on the rate was found to depend on the length of time the carbonyl sulfide was heated before the aldehyde was

TABLE V
RATE OF HYDROGEN SULFIDE SENSITIZED DECOMPOSITION
OF ACETALDEHYDE

Quartz reaction vessel, heated volume 216 cc., dead space 3 cc., temperature 713°K.

Initial pressure, cm. H ₂ S	Initial pressure, cm. CH ₃ CHO	Initial rate, V ₀ cm./min.	V ₀ /H ₂ S	V ₀ /H ₂ S, calcd.
3.99	1.24	0.21	0.053	0.066
4.05	1.40	.24	.059	.070
3.99	2.01	.29	.073	.086
4.03	2.79	.45	.112	.102
4.00	5.65	.56	.140	.144
4.02	8.75	.78	.194	.180
3.77	10.55	.79	.209	.195
4.04	10.94	.84	.208	.198
3.95	14.96	.98	.248	.234
3.97	16.96	1.02	.257	.251
4.11	20.36	1.18	.270	.281
4.01	20.65	1.15	.287	.284
3.88	20.75	1.20	.309	.285
3.89	21.63	1.11	.288	.292
3.98	22.47	1.24	.304	.299
4.03	23.67	1.33	.330	.309
3.95	31.70	1.47	.375	.376
3.99	35.28	1.65	.413	.405
3.98	36.59	1.67	.420	.416
3.80	42.64	1.83	.482	.465
3.92	45.55	1.90	.484	.488
3.98	47.15	2.06	.518	.502
3.98	54.53	2.20	.552	.563
3.84	57.13	2.14	.558	.582
3.92	58.54	2.40	.612	.595
3.97	61.41	2.49	.627	.618
0.63	21.02	0.15	.238	.286
0.75	20.59	.25	.333	.283
2.10	19.65	.66	.314	.275
2.75	20.54	.76	.276	.282
4.01	20.65	1.15	.287	.284
4.97	20.92	1.49	.300	.285
5.89	21.87	1.75	.297	.294
6.80	20.18	1.91	.281	.280
9.25	20.67	2.23	.241	.284
11.38	22.67	3.85	.338	.301
0.90	5.60	0.18	.200	.143
2.02	24.47	.65	.321	.316
2.14	33.63	.85	.397	.392
2.19	16.52	.56	.255	.247
2.62	5.20	.42	.160	.139
10.80	4.70	1.18	.109	.131
11.05	5.25	1.34	.121	.139
16.85	7.38	2.42	.144	.164

admitted to the reaction vessel. Extrapolation to zero preheating time indicated that the carbonyl sulfide had no appreciable effect on the rate. The observed behavior is attributed to the slow decomposition of the added substance into sulfur and carbon monoxide.

The addition of nitric oxide to the reaction mixture gave results of the type indicated in Table VI. It is apparent that the catalytic effect of a

mixture of nitric oxide and hydrogen sulfide is greater than the sum of the effects of these gases taken separately.

TABLE VI
EFFECT OF NITRIC OXIDE AT 713°K.

H ₂ S	Initial pressure, cm. of Hg		Initial rate cm./min.
	NO	CH ₃ CHO	
4.00	0	20.00	1.11
3.88	0.14	20.70	3.27
4.03	0.33	21.12	4.00
4.29	5.89	17.30	4.32
0	3.98	20.67	0.28

The effect of methyl mercaptan and dimethyl sulfide on the rate of decomposition of the aldehyde is of interest both because of the possibility that they are intermediates and because of their similarities in structure to hydrogen sulfide. The rates of decomposition of these substances were too great to study any specific effects due to them. It was noted, however, that the decomposition products catalyzed the aldehyde decomposition more than the corresponding amount of hydrogen sulfide. This may be an effect similar to that found with mixtures of nitric oxide and hydrogen sulfide or it may be due to the presence of some sulfur in the decomposition products of the mercaptan and sulfide added. An analysis of the gaseous products obtained from the complete decomposition of methyl mercaptan showed the composition in per cent. to be 29.2 methane, 7.1 ethane, 9.4 ethylene and 54.2 hydrogen sulfide. The non-gaseous products were not analyzed. The absence of ethane and ethylene in the products of the hydrogen sulfide catalyzed decomposition of the aldehyde indicates that the mercaptan is not an important intermediate.

Water had no appreciable effect on the rate of decomposition of acetaldehyde at 713°K.

The possibility that the reaction was caused by the dissociation of the hydrogen sulfide into hydrogen atoms and hydrosulfide radical followed by the reaction of these substances with the aldehyde to initiate a chain reaction was considered. The equilibrium concentration of the products of such a dissociation as calculated from data in the literature would be sufficient to account for the observed rates but the observed temperature coefficient seems to be too low to be compatible with such a mechanism. None of the mechanisms which we have considered will account for the results quantitatively so they will not be discussed in detail.

Summary

A study has been made of the catalysis of the thermal decomposition of acetaldehyde by hydrogen sulfide. The reaction results in the formation of equivalent amounts of methane and carbon monoxide with no net loss of hydrogen sulfide. The decomposition is homogeneous and the initial rates are given by $-d(\text{CH}_3\text{CHO})/dt = k_1 \cdot (\text{H}_2\text{S})(\text{CH}_3\text{CHO}) + (\text{H}_2\text{S})(\text{CH}_3\text{CHO})/(1 + k_3 \cdot (\text{CH}_3\text{CHO}))$. Values for the constants are given. The effect of temperature on the rate has been studied. The effects of adding hydrogen, sulfur, carbonyl sulfide, methyl mercaptan, dimethyl sulfide, and water to the reaction mixture have also been studied. The results indicate that none of these substances are of importance as intermediate in the hydrogen sulfide catalyzed reaction. Mixtures of nitric oxide and hydrogen sulfide were found to have a greater catalytic effect than the sum of the effects of these gases taken separately.

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