and boiling points of titanium tetrabromide are the higher.

That lead tetrachloride does not appear to form a system of two liquid phases with sulfur dioxide is not surprising in view of the meta-stable nature of the system formed by tin tetrachloride.[1]

In none of the three systems investigated was evidence of compound formation with the solvent discovered. With substances of such low polarity as those in question we should hardly expect to find compounds of as great stability as those which are formed by the highly polar alkali iodides with sulfur dioxide.

Summary

1. The solubility relations of the partially miscible systems formed by titanium tetrabromide and by germanium tetrachloride with liquid sulfur dioxide have been investigated over the entire range of composition.

2. These relations are such as may be expected from considerations of polarity, internal pressure, and melting and boiling points.

3. Lead tetrachloride does not form such a partially miscible system.

4. No evidence of compound formation was discovered.

IOWA CITY, IOWA   RECEIVED JULY 5, 1934

The Induced Decomposition of Acetaldehyde[1]

BY AUGUSTINE O. ALLEN AND DARRELL V. SICKMAN

It recently has been shown[2] that the kinetics of various organic decompositions including that of acetaldehyde can be explained by supposing them to be chain reactions, with free methyl and other organic radicals carrying on the chains. It seemed important to determine whether such chains actually can exist, and whether methyl radicals will react with molecules, such as those of acetaldehyde, with the proper activation energy. This test has been made by heating a mixture of acetaldehyde and azomethane to temperatures around 300°, where the aldehyde is inert, while the azo compound decomposes at a measurable rate, presumably giving free methyl as the initial step in its decomposition.[3]

Experimental

The azomethane was made by the method of Ramsperger[4] and fractionated carefully to remove dissolved air and other impurities. Acetaldehyde (Eastman best grade) was purified by fractionating several times before using. The vapors of these compounds were let through stopcocks into an evacuated one-liter bulb, and allowed to stand overnight to ensure thorough mixing. It was found that if any traces of air were present a reaction, presumably polymerization of the aldehyde, would occur resulting in the formation of a reddish water-soluble tar; but with greater precautions to exclude air, the mixture could be kept indefinitely. In making runs, a portion

of the mixture would be let into another bulb, connected to the reaction vessel through a three-way stopcock, its other lead connecting the reaction vessel directly to the pump. The gas would then be admitted to the evacuated reaction flask, and pressure allowed to equalize before closing the stopcock again; the reaction could be followed on a mercury manometer connected to the reaction flask, while another manometer on the admission bulb gave the initial pressure. The reaction vessel was a 200-cc. Pyrex bulb. Another bulb of the same size was also used, packed with short pieces of 4 mm. (o. d.) Pyrex tubing, with ends fire-polished; the surface was increased 12- or 13-fold. Between runs the reaction bulb would be evacuated to 10^{-4} mm. or less. A mercury diffusion pump backed by an oil pump was used. The oil in the latter had to be changed frequently, acetaldehyde dissolving readily in it and eventually preventing the attainment of a good vacuum. The reaction bulb was in an electrically heated air-bath, whose temperature was kept spatially uniform by separate adjustments of heating units at its ends, and temporally constant to $\pm 0.5°$ by a de Khotinsky bimetallic regulator. Temperatures were measured by an iron–constantan thermocouple calibrated in boiling sulfur.

In a preliminary experiment, acetaldehyde was found to show no pressure change on standing overnight at 300°. To test the effect of mercury vapor, a drop of mercury was introduced into the reaction bulb together with the aldehyde, but once the mercury had distilled out again it was seen that no aldehyde had decomposed. The mercury catalyzed decomposition of aldehyde reported by Kassel[5] was thus not observed; Kassel's pressure increases are probably to be explained simply by the rather slow evaporation of the mercury droplets which are introduced in his experiments. The azomethane was found to decompose at rates agreeing with those of Ramsperger.[4]

(1) A preliminary notice of this work appeared as a Communication to the Editor, THIS JOURNAL, 56, 1251 (1934).

(2) F. O. Rice and Herzfeld, ibid., 56, 284 (1934).

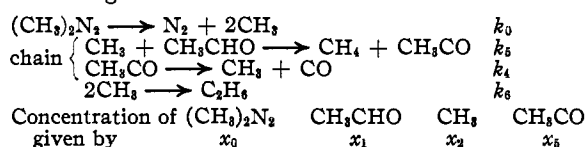(3) Kassel, "The Kinetics of Homogeneous Gas Reactions," p. 199.

(4) Ramsperger, THIS JOURNAL, 49, 912 (1927).

(5) Kassel, J. Phys. Chem., 34, 1171 (1930).

Results and Discussion

Experiments were done at varying temperatures, pressures, and compositions of the mixture. In many cases the runs were allowed to proceed to completion, and the aldehyde was then found, in the empty vessel, to be entirely decomposed, the final pressure reached being double the total initial pressure. (The actual measured ratio was in all cases 1.93, but a correction for the effect of the volume of manometer and connections external to the reaction vessel effectively raised this to 2.0.) The first run made with each of the bulbs used was erratic; all the other experiments are summarized in Table I, which gives the percentage of azomethane in the mixture used, the total initial pressure and the rate of increase of pressure extrapolated to zero time. Table II gives complete data for two typical runs.

Before describing the treatment of these results, let us outline the theory of the expected chain reaction. The treatment is very similar to that given by Rice and Herzfeld[2] for pure acetaldehyde, and applies only to the initial stages of the reaction. We have a series of reactions occurring

$$(CH_3)_2N_2 \longrightarrow N_2 + 2CH_3 \qquad k_0$$
$$\text{chain} \begin{cases} CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO & k_5 \\ CH_3CO \longrightarrow CH_3 + CO & k_4 \end{cases}$$
$$2CH_3 \longrightarrow C_2H_6 \qquad k_6$$

Concentration of $(CH_3)_2N_2$ CH_3CHO CH_3 CH_3CO
given by x_0 x_1 x_2 x_5

We follow the notation of Rice and Herzfeld in representing the rate constants for the various reactions, and the concentrations of the substances involved. We also, following them, assume that the reaction between CH_3 and CH_3CO radicals is negligibly slow compared to that between two CH_3's (due to the low concentration of CH_3CO). The concentration of the two radicals will soon become steady, so that

$$dx_2/dt = 2k_0x_0 - 2k_6x_2{}^2 + k_4x_5 - k_5x_2x_1 = 0$$
$$dx_5/dt = k_5x_2x_1 - k_4x_5 = 0$$

Combining these equations, one finds $x_2 = \sqrt{k_0x_0/k_6}$. The rate of disappearance of aldehyde is $-dx_1/dt = k_5x_2x_1 = k_5\sqrt{k_0/k_6}\,x_1x_0{}^{1/2}$.

As we are working at low percentages of azomethane, this rate will be nearly equal to the observed rate of increase of pressure. Hence we define our rate constant K by $K = (dP/dt)_0/P_{ald}.P_{az}.{}^{1/2}$, where the P's are the partial pressures of aldehyde and azomethane at the beginning of the run. The calculated values are given in the last column of Table I; it is seen that over a considerable range of pressures and compositions K for each temperature is as constant as could be

TABLE I

Expt.	Temp., °C.	% Az.	P_0, mm.	$(dP/dt)_0$, mm. per min.	$K \times 10^3$, mm.$^{-1/2}$ min.$^{-1}$
2	328.7	9.18	100	12	44.5
3	328.7	9.18	50.5	4.5	46.4
4	328.7	1.25	197	16	52.3
5	328.7	4.08	384	100	68.0
6	328.7	4.08	112	12	52.2
7	328.7	4.08	36	2.25	54.0
8	302.8	4.08	298	12.5	12.4
9	302.8	4.08	101	3.0	15.1
10	302.8	4.08	33.8	0.50	13.1
11	268.3	4.08	331.5	1.3	1.11
12	268.3	4.08	106.5	0.30	1.40
13	268.3	4.08	39.3	.06	1.25
14	313.3	1.20	334	30	4.6
15	313.3	1.20	111	3.2	2.5
16	313.3	1.20	55.5	1.0	2.2
17	259.4	1.20	383	0.625	0.77
18	259.4	1.20	249.5	.37	.872
19	244.8	1.20	229	.092	.245
20	244.8	1.20	147	.052	.266
22	312.6	1.20	228	3.7	9.95
23	312.6	1.20	172	2.6	10.7
24	272.4	1.20	205.5	0.113	0.354
25	272.4	1.20	151	.10	.496
26	336.8	1.20	114	4.29	32.3
27	336.8	1.20	87	2.89	32.8
28	336.8	1.20	183	10.1	37.6
29	295.5	1.20	137	0.35	2.09
30	294.0	1.20	167	.63	2.7
31	293.0	1.20	124.5	.436	2.9

The experiments after No. 20 are with increased surface.

TABLE II

Expt. No. 6		Expt. No. 18	
Time, min.	Pressure, mm.	Time, min.	Pressure, mm.
0	112	0.50	250
0.25	114.5	2	250.5
.75	120.5	5	252
1.25	127	7	253
1.75	131	10	254
3	144	15	256
5	158	20	257.5
7	169.5	25	259.5
9	177.5	30	261
12	187	35	262.25
17	196	100	282.25
64	214	120	288
104	217	150	296.25
123	217	170	301
		452	358
Ratio of final pressure to initial: 217/112 = 1.937		483	363
		761	400.5
		787	402.5
		1471	450.75
		1567	454

Not carried to completion

Table III

Expt.	$P_{ald.}/P_{az.}^{1/2}$	Temp., °C.	λ
2	30.0	328.7	22
5	93.0	328.7	69
10	23.5	302.8	27
15	94.9	313.3	91
19	136	244.8	500

expected in view of the experimental errors, of which the worst was probably the extrapolation of dP/dt to zero time. No other expression for the rate was found which would give constants nearly as good.

In the figure, log k is plotted against $1/T$. The points for the unpacked reaction vessel fall on a straight line which yields an activation energy $E = 39.4 \pm 1.6$ Cal. Now, we have $K = k_5 \sqrt{k_0/k_6}$; so that considering the exponentially temperature-dependent parts of these rate constants, $E = E_5 - \frac{1}{2}E_6 + \frac{1}{2}E_0$. But E_0 is known to be 51.2 Cal., so $E_5 - \frac{1}{2}E_6 = 13.8$ Cal. This is to be compared with the value found for the same quantity on the theory of Rice and Herzfeld[2] from the kinetics of the decomposition of pure aldehyde. There we have $E_5 - \frac{1}{2}E_6 = E_{ald.} - \frac{1}{2}E_1$, where $E_{ald.}$ is the over-all activation energy for the decomposition of aldehyde and E_1 that for the initial step of the decomposition—the dissociation of the aldehyde into radicals. The best value for $E_{ald.}$ is 48 Cal.,[6] while E_1 has been found to be 70 $\pm$ 3.[7] Thus $E_5 - \frac{1}{2}E_6 = 13$, in good agreement with our value.

If the decomposition of azomethane were a chain reaction, the expression for K would remain unchanged, but k_0 would then be the rate of the initial step in the azomethane decomposition, which would have a higher activation energy than the observed over-all value 51.2. Thus the fact that we get agreement with Rice and Herzfeld's theory for acetaldehyde by using 51.2 for E_0 indicates that the decomposition of azomethane is not a chain reaction while that of acetaldehyde is. The errors involved are large enough to mask a considerable discrepancy, however.

Leermakers[8] from the temperature coefficient of the photolysis of acetaldehyde, gets a definitely lower value than ours for a quantity which is similar to $E_5 - \frac{1}{2}E_6$. But he is dealing with a different E_6, for in the photolysis, the radicals disappear by the reaction $CH_3 + CHO \longrightarrow CO + CH_4$. In the present case, no CHO radicals are ever formed, so the CH_3's disappear by combination with themselves. We can then conclude that the reaction of CH_3 with CHO has a higher activation energy than the

bimolecular association of two methyls, though the latter reaction must have a much larger steric or probability factor. The value of $E_5 - \frac{1}{2}E_6$ from the decomposition of pure acetaldehyde agrees with our value rather than with Leermakers'; this must mean that at the high temperature used in this case the CHO radical is unstable, as postulated by Rice and Herzfeld;[2] it quickly decomposes to CO and H, leaving the methyl to disappear by combination with itself.
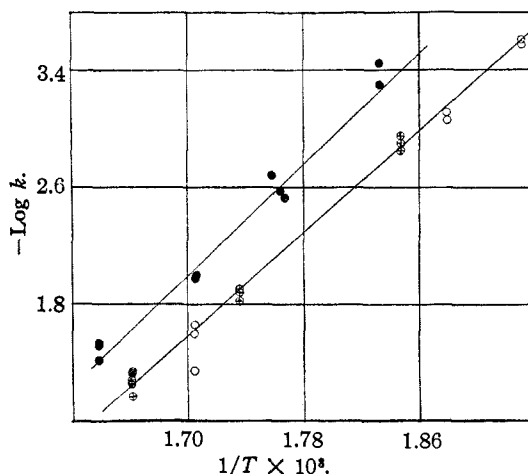

Fig. 1.—○, 1.20% azomethane; ⊘, 1.25%; ⊕, 4.08%; ⊗, 9.18%; ●, increased surface.

The effect of packing the reaction vessel with pieces of 4-mm. tubing is to reduce the rate by more than half; this is shown strikingly in the figure. The effect must be due to termination of the reaction chains on the walls; as the chains in this reaction are longer the lower the temperature, the inhibition should be greater at low temperatures; this is seen to be actually the case. Shortening of the chains was shown also by the fact that in these runs the aldehyde was only about 60% decomposed. In view of the geometrical complexity of packed flasks, it seems impossible to work out any quantitative theory; but there is one point worth remarking. If the effect of added surface is merely to terminate chains, the important quantity is the average distance of the gas molecules from the wall, not the surface-volume ratio. Now, Fletcher and Hinshelwood[6] found that acetaldehyde decomposed 15% slower in a packed flask than in an unpacked one, which is a much smaller effect than ours, although on the Rice–Herzfeld theory they were dealing with longer chains than we. But although their surface–volume ratio was of the same order as ours, they had a larger flask packed with larger tubing, so that the average distance of the gas molecules from the wall was considerably greater

(6) Fletcher and Hinshelwood, Proc. Roy. Soc. (London), A141, 41 (1933). These authors report slightly different activation energies for different pressures, but it appears unlikely that these differences are beyond the range of experimental error.

(7) Rice and Johnston, This Journal, 56, 214 (1934).

(8) Leermakers, ibid., 56, 1537 (1934).

in their case. If the chain theory for the decomposition of aldehyde is correct, we should thus expect to be able to reduce the rate of the reaction very considerably by packing the reaction vessel with smaller tubing than Fletcher and Hinshelwood used. Probably an even better test would be to run the reaction in vessels composed of long lengths of coiled-up tubing of different sizes, which should give results more amenable to theoretical treatment.

The behavior to be expected theoretically for our reaction during a run is somewhat complicated, as the azomethane and aldehyde are decomposing at different rates. A formula can be obtained from which one should be able to calculate, from the behavior during the run, the rate at which the azomethane is going, provided the accumulation of reaction products be assumed not to affect the rate of reaction in any way. These calculations were carried through for several runs, but are not given in detail, as it was found that a slight error in the rate measured at any time produces a relatively enormous change in the calculated value of the azomethane rate constant, so that the latter can be found to a rough order of magnitude only. It was found to agree in order of magnitude with the rate obtained for pure azomethane at the same pressure and temperature; this was of course to be expected.

The chain length is the ratio of the aldehyde and azomethane decomposition rates and is given by $(K/k_0)P_{ald.}/P_{az.}^{1/2}$. As the temperature coefficient of k_0 is larger than that of K, the chain length decreases with rising temperature. At the pressures of azomethane used, we will have approximately $k_0 = 10^{15.67} e^{-51,200/RT}$; and $K = 10^{11.26} e^{-39,400/RT}$ (K is now in sec.$^{-1}$ mm.$^{-1/2}$). Then we readily find, if λ is the chain length, $\log \lambda = \log (P_{ald.}/P_{az.}^{1/2}) - 4.41 + (11,800/4.58\,T)$. Some typical values of λ are given in Table III.

The study of the reactions of methyl radicals with organic compounds is seen to be of considerable interest. It is hoped to make further studies along these lines using ethyl and possibly larger radicals as well as methyl.

Summary

The presence of decomposing azomethane induces decomposition in acetaldehyde. The kinetics of the reaction have been studied, and the results explained on the theory that the methyl radicals from the azomethane start a chain-type decomposition in the aldehyde. The temperature coefficient agrees with that expected from the theory, advanced by F. O. Rice and Herzfeld, that the pyrolysis of pure acetaldehyde is also a chain reaction.

The Slow Oxidation of Propane

BY ROBERT N. PEASE AND WENDELL P. MUNRO[1]

In a previous investigation of the non-explosive reaction of propane with oxygen,[2] it was concluded as a result of gas-analytical data alone that there were three main types of reaction: (1) a decomposition of the hydrocarbon to olefin, and methane or hydrogen at temperatures much below the normal, which must have been induced by the oxidation reactions, e. g.

$$M^* + C_3H_8 \longrightarrow C_2H_4 + CH_4 + M$$

(2) an oxidation yielding olefin and liquid oxidation products, e. g.

$$C_3H_8 + O_2 \longrightarrow C_2H_4 + HCHO + H_2O$$

(3) an oxidation yielding carbon monoxide and a liquid oxidation product, e. g.

$$C_3H_8 + 2O_2 \longrightarrow CH_3CHO + CO + H_2O$$
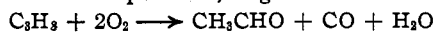
It was further concluded that the oxidation reactions (2) and (3) are of the chain type since— (1) the reaction is highly auto-accelerative; (2) it is suppressed by inert foreign gases in certain cases; (3) it is suppressed by a glass packing; (4) the kinetics follow no simple scheme. The purpose of the investigation here reported was to amplify the original work by determining liquid as well as gaseous products, with a view to fixing more definitely the nature of the oxidation reactions (2) and (3).

Experiments were carried out by the flow

(1) Du Pont Fellow in Chemistry, Princeton University, 1932–1933.

(2) Pease, THIS JOURNAL, 51, 1839 (1929).