

was found to alter greatly the vapor pressure of the magnesium bromide-ethyl ether system. This fact was advanced as a possible explanation

for the low values reported in the literature by several authors.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of Iodine on the Rates of Decomposition of Formaldehyde, Acetaldehyde and Propionaldehyde

BY G. K. ROLLEFSON AND R. FRANCIS FAULL

In a previous note¹ we have presented data which show that the accelerating effect of iodine in a number of decompositions of simple organic molecules is due to a cycle of reactions involving destruction and re-formation of the iodine molecules. That work has been extended for the aldehydes so that now it is possible to give the mechanism in detail. These systems were found to be more complex than was indicated previously in that the rate of disappearance of aldehyde was definitely greater than the rate of reaction between the corresponding alkyl iodide and hydrogen iodide as calculated from Ogg's data² on those reactions. In fact as the temperature was lowered from the range discussed before this discrepancy increased until with acetaldehyde (to take an extreme case) the observed rate was several times as large as the one calculated on our earlier assumptions. In this paper we shall show that this discrepancy may be accounted for if we take into consideration the free radicals and iodine atoms which are present under the experimental conditions.

The reaction vessel was of Pyrex, cylindrical in shape, 15 cm. long with plane windows at both ends; the volume was approximately 250 cc. The vessel was mounted in an electric furnace that was fitted with windows so as to allow a beam of light to be directed lengthwise through the reaction vessel. The temperature was measured by a chromel-alumel thermocouple that was placed in a well extending into the reaction vessel in such a manner as not to lie in the optical path through the vessel. The furnace could be kept constant within a degree by manually regulated rheostats. The pressure was measured by a click gage, used as a null instrument, and a system that consisted of a mercury manometer and a sulfuric acid manometer connected so the mercury manometer could be used for high pressures and the sulfuric acid manometer for low pressures. The reaction vessel was connected to a vacuum line and to an iodine storage bulb, each through a heated glass valve. The iodine storage bulb was immersed in a small oil-bath that could be heated to distil iodine into the reaction ves-

sel. The connecting tubing to the click gage and glass valves was capillary, wound with resistance wire and electrically heated to prevent the condensation of iodine. The dead space in the connections was about 2 cc.

The concentration of iodine during the course of a reaction was determined by measuring the intensity of a beam of light which passed through the reaction vessel. The light source was a thirty-two candle power automobile lamp connected through a resistance to a storage battery. A Corning glass filter No. 428 was placed between the lamp and the furnace window. The light transmitted by this filter is in the region of the maximum absorption by iodine. It has been pointed out by Cuthbertson and Kistiakowsky³ that good results may be obtained in measuring the absorption of iodine with a blue filter while without the filter the effect of foreign gases on the absorption of iodine would cause a large error. The intensity of the beam was measured by a Weston Photronic Cell, No. 594, connected to a D'Arsonval galvanometer.

The acetaldehyde and propionaldehyde were taken from the center fractions of carefully dried Eastman Kodak Co. stock. Each sample was distilled several times and stored in three-liter bulbs connected to the vacuum line. No trouble from polymerization was experienced in storing the gases. The formaldehyde was prepared by heating trioxymethylene in a 500-cc. flask in an oil-bath. Above 200° the amount of polymer that exists in gaseous formaldehyde is very small; so no polymer could have existed in our experiments at 500°. The methyl iodide was prepared and stored similarly to the acetaldehyde. The iodine was a Merck reagent.

In order to determine the concentration of iodine present during the course of an experiment, it was necessary to make a calibration of the intensity measuring system. This was done by introducing certain amounts of iodine into the reaction vessel and by taking both the pressure reading and the galvanometer deflection. A curve could be constructed giving the relation of the light absorbed to the pressure of the iodine. To compensate for the small changes in light intensity and absorption in the reaction vessel due to tarring the galvanometer deflection with no iodine in the system was adjusted by varying the current passing through the light source.

The general procedure during a particular experiment was to introduce a certain desired amount of iodine vapor and read the pressure with the sulfuric acid manometer. The aldehyde, under higher pressure, was then introduced rapidly and an electric clock started simultaneously.

(1) Faull and Rollefson, *THIS JOURNAL*, **58**, 1755 (1936).

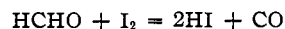
(2) Ogg, *ibid.*, **56**, 526 (1934).

(3) Cuthbertson and Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

Pressure readings could be obtained conveniently with the mercury manometer at one-half or one minute intervals. In order to find the initial pressure of aldehyde a graphical extrapolation to zero time was made. This value was corrected for the iodine present and also for the initial rapid increase due to the formation of three molecules from one of aldehyde and one of iodine. This latter correction was necessary because in every case the iodine had disappeared almost completely before the first pressure reading could be made.

In regard to the measurements on the iodine during the steady state it was observed that the concentrations were very low. In no case was the concentration over 5% of the initial iodine. The tarring that inevitably accompanies a reaction of this type made an exact determination impossible. To avoid these uncertainties we assumed in our calculations that the concentrations of hydrogen iodide and alkyl iodide were equal to the iodine added during the steady state. No great error could have been introduced by this assumption. When the reactions were complete the observed end-point was never quite equal to the theoretical end-point. This discrepancy was caused by a simultaneous condensation reaction and amounted to about 10 or 15% in the pressure reading. The magnitude of the

composition as shown by the curves in Fig. 1 although the iodine color disappears rapidly. Assuming that iodine reacts with formaldehyde according to the equation



the limiting rate of any cycle of reactions is the rate of regeneration of iodine by the bimolecular decomposition of hydrogen iodide. This rate may be calculated from the work of Bodenstein as summarized by Kassel⁵ the equation being

$$d(\text{I}_2)/dt = 5.65 \times 10^{12} T^{1/2} e^{-46,116/RT} (\text{HI})^2 \text{ cc./mole/sec.}$$

At 500°, expressing the concentrations in cm. and the time in minutes, this equation reduces to

$$d(\text{I}_2)/dt = 1.74 \times 10^{-3} (\text{HI})^2$$

On the introduction of 1 cm. of iodine the pressure of hydrogen iodide would become 2 cm., and the time required to produce a 1-cm. change is two hours and twenty-four minutes. This rate is only about one-fiftieth as fast as the thermal

decomposition of formaldehyde, so no appreciable catalytic effect of iodine should be observed. Also, since there is no observed effect other than the disappearance of iodine, we may conclude that there is no reaction between formaldehyde and hydrogen iodide that is comparable to the thermal decomposition.

Acetaldehyde and Propionaldehyde.—The decompositions of acetaldehyde and propionaldehyde into methane and carbon monoxide and ethane and carbon monoxide, respectively, at temperatures above 350° are markedly accelerated by the addition of a small amount of iodine. Above 400° these systems change rapidly to a condition in which the concentration of free io-

dine is so low that it cannot be detected by absorption measurements. In this state the net reaction is the decomposition of the aldehyde. As the aldehyde concentration is decreased a point is reached at which the iodine color begins to reappear and as the aldehyde concentration decreases the free iodine concentration increases until when the aldehyde is completely decomposed all the original iodine is in the free state. At

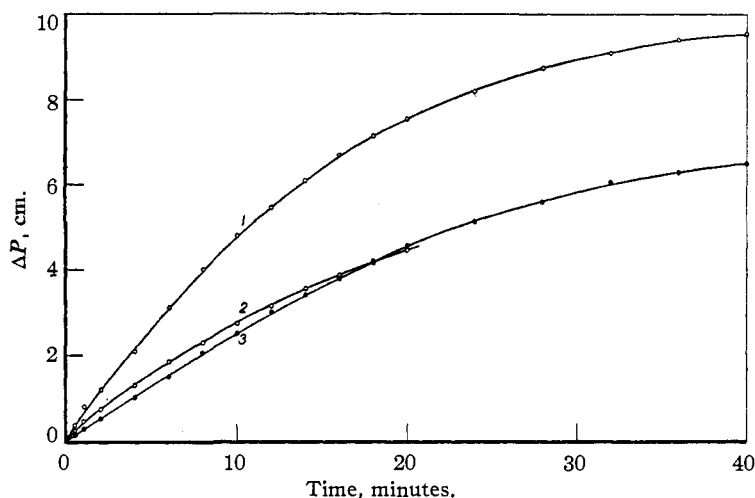


Fig. 1.—Curves 1 and 2 show the pressure increase in reactions with the initial pressure of formaldehyde 14.00 cm. and 11.20 cm., respectively. Curve 3 shows the pressure increase in a reaction mixture containing 11.38 cm. of formaldehyde and 1.06 cm. of iodine. The temperature was 500° in all experiments.

difference was distributed quite randomly through the different runs. As nothing is known about this side reaction no correction was made in the calculation.

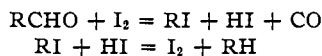
Results and Discussion

Formaldehyde.—Formaldehyde is known to decompose into hydrogen and carbon monoxide at temperatures in the neighborhood of 500° and above at an appreciable rate.⁴ On introducing iodine to the thermal reaction mixture at 500° there is no noticeable increase in the rate of de-

(4) Fletcher, *Proc. Roy. Soc. (London)*, **A146**, 357 (1934).

(5) Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932, p. 150.

lower temperatures the free iodine is not removed so completely although at 350° it is still less than 5% of the amount originally added. Furthermore our measurements show that this low concentration is constant (within 10%) so that we may consider that we are dealing with a steady state in which the net result is a catalysis. If we assume that the catalysis is due to the reactions



then the rate determining step will be the one between the alkyl iodide and hydrogen iodide. The rates of reaction between methyl iodide and hydrogen iodide and ethyl iodide and hydrogen iodide have been studied by Ogg over a temperature range from 250 to 320°.² If we extrapolate his rate equations to temperatures of the systems under consideration we find the results tabulated in Tables I and II. The first table shows the data for a typical experiment with acetaldehyde. The third column gives the observed rate and the fourth the rate calculated assuming that every molecule of iodine has reacted to give one of methyl iodide and one of hydrogen iodide. The

TABLE I
ACETALDEHYDE WITH 0.41 CM. OF IODINE AT 364°

Time, min.	Press. ald., cm.	Obsd. rate, cm./min.	Calcd. rate, cm./min.	Diff., cm./min.
2	17.02	1.31	0.20	1.11
4	14.67	1.01	.20	0.81
6	13.02	0.79	.20	.59
8	11.52	.68	.20	.48
10	10.57	.59	.20	.39
12	9.17	.49	.20	.29
14	8.27	.41	.20	.21

TABLE II
PROPIONALDEHYDE WITH 0.42 CM. OF IODINE AT 350°

Time, min.	Press. ald., cm.	Obsd. rate, cm./min.	Calcd. rate, cm./min.	Diff., cm./min.
2	12.64	1.10	0.44	0.66
4	10.69	0.90	.44	.46
6	9.09	.77	.44	.33
8	7.49	.68	.44	.24
10	6.29	.57	.44	.13
12	5.09	.44	.44	.00

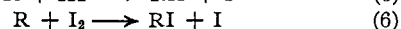
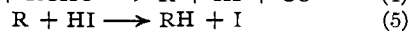
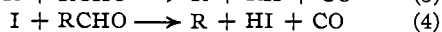
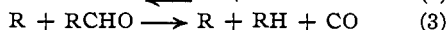
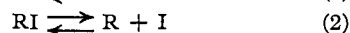
difference tabulated in the last column shows a marked trend with the aldehyde pressure. Similar results were obtained with propionaldehyde as shown in Table II, although in this case the discrepancy between the observed and calculated rates is less at all pressures than with acetaldehyde. At low aldehyde pressures the system goes out of the steady state and the calculated rates

are no longer valid; so the discrepancy cannot be followed to its limiting value.

In seeking an explanation for this high rate of reaction we turned to a consideration of the mechanism given by Ogg for the reactions between the alkyl iodides and hydrogen iodide. His rate laws are of the form

$$-\frac{d(\text{RI})}{dt} = k_1 (\text{RI}) (\text{HI}) + k_2 \frac{(\text{RI})(\text{HI})}{(\text{HI}) + (\text{I}_2)}$$

In this equation the first term is attributed to a simple bimolecular reaction and the second term is due to a series of reactions involving dissociation of the alkyl iodide into an iodine atom and an alkyl radical as the primary step. Now it has been shown by Leermakers,⁶ Allen and Sickman⁷ and Fletcher and Rollefson⁸ that the decomposition of acetaldehyde is catalyzed at these temperatures by free radicals. Therefore if Ogg's mechanism is correct the high rate of reaction of the aldehyde might be accounted for as due to the catalysis by the free radicals produced in the thermal dissociation of the methyl iodide. In order to test this hypothesis several experiments were performed in which a small amount of methyl iodide was added to the acetaldehyde. Some reaction occurred but it was only about one-tenth as fast as with a corresponding amount of iodine. The observed rates in these experiments were found to be proportional to the square root of the pressure of the methyl iodide as it should be if the free radical mechanism were correct. Similar tests with hydrogen iodide showed no marked effect. This result shows that it is necessary to assume that either there is some source of free radicals other than the decomposition of methyl iodide or the iodine atoms present have a marked catalytic action for the decomposition of the aldehyde. We have tested a number of possibilities but the following set of reactions is the most completely in accord with the experimental facts, while the system is in the steady state.



In this set of reactions it is to be noted that the sum of (4) and (5) is essentially the decomposi-

(6) Leermakers, *THIS JOURNAL*, **56**, 1537 (1934).

(7) Allen and Sickman, *ibid.*, **56**, 2031 (1934).

(8) Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936).

tion of the aldehyde catalyzed by iodine atoms. Also according to Ogg the specific reaction rates of (5) and (6) are equal and since in our experiments the concentration of hydrogen iodide was always at least twenty times that of iodine, (6) is of minor importance and is included only for the sake of completeness. If we apply the usual methods of equating the rates of formation and removal of the intermediates R and I we find that the above set of reactions leads to the equation

$$k_1(I_2) + 2k_2(RI) = 2k_2'(R)(I) + k_1'(I)^2$$

in which k_1' and k_2' represent the specific reaction rates for the reverse of (1) and (2), respectively, and k_1 and k_2 refer to the direct reactions. From an inspection of the reactions listed it may be seen that the net over-all reaction is the decomposition of the aldehyde. Under such conditions the equilibria in reactions (1) and (2) will not be disturbed, therefore we may write

$$\begin{aligned} k_1(I_2) &= k_1'(I)^2 \\ k_2(RI) &= k_2'(R)(I) \end{aligned}$$

and

$$\begin{aligned} (I) &= \sqrt{K_1(I_2)} \\ (R) &= K_2 \frac{(RI)}{(I)} = K_2(RI) / \sqrt{K_1(I_2)} \end{aligned}$$

in which K_1 and K_2 are the equilibrium constants for (1) and (2), respectively. Calculating the rate of disappearance of aldehyde by these reactions we have

$$\begin{aligned} -\frac{d(\text{RCHO})}{dt} &= k_3 \frac{K_2(RI)(\text{RCHO})}{\sqrt{K_1(I_2)}} + k_4(\text{RCHO}) \sqrt{K_1(I_2)} \\ &= (\text{RCHO}) \left[\frac{k_3 K_2(RI) + k_4 K_1(I_2)}{\sqrt{K_1(I_2)}} \right] \end{aligned}$$

In any given experiment when the system has reached the steady state (RI) and (I_2) are constant and proportional to the initial amount of iodine. Let $(I_2)_0$ equal the pressure of iodine added and α be the fraction remaining as I_2 with $1 - \alpha$ the fraction as RI and HI. Then our equation becomes

$$-\frac{d(\text{RCHO})}{dt} = (\text{RCHO})(I_2)_0^{1/2} \left[\frac{k_3 K_2(1 - \alpha)}{K_1^{1/2} \alpha^{1/2}} + k_4 K_1^{1/2} \alpha^{1/2} \right]$$

All the quantities contained within the brackets are constants when the system is in the steady state so the rate of removal of aldehyde is proportional to the aldehyde pressure and the square root of the initial iodine pressure. The only one of these quantities which could be considered as having a possibility of varying in the steady state is α . The absolute value of α will depend upon

the relative rates of formation and disappearance of the iodine. The rate of formation depends upon the concentrations of the alkyl iodide and hydrogen iodide according to the law given by Ogg

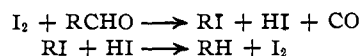
$$\frac{d(I_2)}{dt} = k_1(RI)(HI) + k_2 \frac{(RI)(HI)}{(HI) + (I_2)}$$

In what we have called the steady state $(RI) = (HI)$ and both are constant and approximately equal to the iodine added. The rate expression just given therefore reduces to $((I_2)_0)$ is the iodine originally added)

$$d(I_2)dt = k_1(I_2)_0^2 + k_2(I_2)_0$$

and since under the conditions of our experiment the second term is much larger than the first we may say that the rate of formation of iodine is approximately proportional to the amount originally added. In the steady state the rate of disappearance of iodine, whatever law it follows, is the same as its rate of formation. Under these conditions the only reactant which is changing appreciably is the aldehyde, therefore if the rate is to depend on α and the aldehyde pressure it must do so in such a way that the effect of any change in the aldehyde pressure is offset by a corresponding change opposite in sign in α . Our measurements in the steady state are sufficiently accurate to show that this is definitely not the case but that α is independent of the aldehyde as long as the steady state conditions exist. Since there is no other variable we must conclude the α is constant.⁹ The breakdown of the steady state at pressures of 5-6 cm. of acetaldehyde or 3-5 cm. of propionaldehyde corresponds to the deviation of α from constancy.

The rate equation just derived does not give the total rate of disappearance of aldehyde but only that part due to the presence of free radicals and iodine atoms. There still remains a certain amount of decomposition according to the mechanism



These reactions contribute a term $k(RI)(HI)$ which is identical with the first term of the rate law given by Ogg for the reaction between the alkyl iodide and hydrogen iodide. The second term of Ogg's law corresponds to reactions which have already been taken into account in the

(9) A law for the disappearance of iodine which would fit these conditions is $-d(I_2)/dt = k\alpha(I_2)_0(\text{RCHO})/1 + k'(\text{RCHO})$ but we have no direct evidence for such a law nor is it obvious how such a law could be obtained.

mechanism involving free radicals. The total rate of disappearance of aldehyde may be written

$$-d(\text{RCHO})/dt = k(\text{RI})(\text{HI}) + k'(\text{RCHO})(\text{I}_2)_0^{1/2}$$

where the first term may be calculated from Ogg's data and the second term is that due to the free radical mechanism already discussed with all the constants grouped together in k' . In order to test this expression we have determined the rates of reaction in the region where the iodine is principally in the form of alkyl iodide and hydrogen iodide. The observed rates for a typical experiment are given in column three, Table III. The next column gives the difference between this rate and the $k(\text{RI})(\text{HI})$ as calculated from Ogg's equation. The last column gives the values of k' assuming our rate law to hold. In Tables IV and V the results are given for acetaldehyde and propionaldehyde, respectively, in a number of

experiments with different amounts of iodine added. From the constancy of the value of k' the results may be said to be in agreement with the rate law as given above.

The equation we have been discussing is strictly valid only when the system is in what may be called a steady state with respect to iodine, *i. e.*, the amount of free iodine present is essentially constant. This condition is fulfilled when the ratio of aldehyde to iodine added is large. Toward the end of an experiment when this ratio is becoming small the values of k' decrease due to the increase in α . Experimentally it was found that the decrease in k' coincided with the return of the iodine color.

On the basis of our mechanism the apparent order of the reaction with respect to aldehyde will depend on the relative importance of the two terms in the rate law. Thus with acetaldehyde the second term accounts for the major portion of the rate and therefore the reaction appears to be of approximately first order with respect to acetaldehyde. With propionaldehyde the first term is more important and therefore the apparent order with respect to propionaldehyde is somewhat less than the first order.

Summary

The addition of iodine markedly accelerates the decompositions of acetaldehyde and propionaldehyde but does not affect the decomposition of formaldehyde appreciably. It is shown that these effects can be explained by assuming that the iodine reacts with the aldehyde first and this step is followed by two parallel sets of reactions. The first is a simple bimolecular reaction of the alkyl iodide and hydrogen iodide formed from the above-mentioned reaction. The second is a series of reactions involving the free radicals and iodine atoms produced by the thermal dissociations of the alkyl iodide and the residual iodine. Detailed mechanisms are presented and it is shown that they fit the experimental facts.

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TABLE III

ACETALDEHYDE WITH 1.38 CM. OF IODINE AT 364°
The value of $k(\text{RI})(\text{HI})$ is 0.24 cm./min.

Time, min.	Press. I_2 , cm.	Obsd. rate, cm./min.	$k'(\text{RCHO})(\text{I}_2)_0^{1/2}$	k'
2	14.41	1.57	1.33	0.0785
4	11.81	1.30	1.06	.0764
6	9.31	1.11	0.87	.0795
8	7.21	0.90	.66	.0779
10	5.71	.65	.41	.0610

TABLE IV

ACETALDEHYDE AT 364°

Press. I_2 , cm.	Range of ald. press., cm.	$k(\text{RI})(\text{HI})$	Average $k'(\text{I}_2)_0^{1/2}$	Average k'
0.41	17.02-8.27	0.021	0.056	0.086
.52	16.59-5.69	.034	.070	.097
.71	15.40-5.95	.063	.082	.098
.95	14.55-6.65	.113	.086	.088
1.38	14.41-5.71	.238	.092	.078

TABLE V

PROPIONALDEHYDE AT 350°

Press., I_2 , cm.	Range of ald. press., cm.	$k(\text{RI})(\text{HI})$	Average $k'(\text{I}_2)_0^{1/2}$	Average k'
0.42	12.64-5.09	0.055	0.081	0.125
.60	13.35-7.40	.112	.087	.112
.77	11.67-4.27	.187	.105	.119
.80	7.85-3.00	.199	.105	.117
.81	10.18-4.33	.202	.112	.125
1.21	7.37-3.42	.455	.144	.131