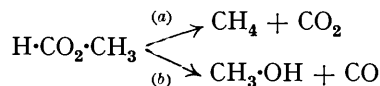


(The formic acid was treated repeatedly with anhydrous copper sulphate and then distilled. Analysis showed it to contain 4.6% of water.) The decomposition of the formic acid is largely, though possibly not entirely, heterogeneous at this temperature. In a vessel packed with silica spheres the rate was about seven times as great as in the unpacked vessel: an appreciably greater acceleration would have been expected if the reaction were entirely heterogeneous. But since surfaces vary not only quantitatively but also qualitatively, the result is inconclusive. The influence of iodine on the reaction in the packed bulb was negligible.

Formic acid decomposes to give either hydrogen and carbon dioxide or water and carbon monoxide. It might therefore be expected that methyl formate would undergo the analogous changes :



It has been stated that formaldehyde can be formed at high temperatures but no trace has been found in any of our experiments.

The two processes (a) and (b) are both catalysed by iodine, which also influences the further decomposition of the methyl alcohol formed in (b).

The methyl formate used was dried and fractionated; b. p. 31.5—32.0°.

The following table indicates the extent to which the initial rate of decomposition is increased by iodine. The catalyst concentration is given as mm. of decomposed *iso*-propyl iodide, the actual pressure of iodine being approximately one-third of this.

Temperature, 451°; initial pressure of formate = 100 mm.					
Catalyst, mm.	6	11	21.5	33.5	46.5
Ratio of rates (with I ₂)/(without I ₂)	20	25	38	48	54

Kinetically the reaction is by no means simple. There is a clear indication that the decomposition occurs in consecutive stages. Furthermore, the total increase of pressure at the end of the change varies with the amount of catalyst present. The following figures are typical of the numerous experiments made.

Temperature, 451°; initial pressure of formate, 114 mm.; catalyst, 8 mm.								
Time.	Change in press., mm.	Time.	Change in press., mm.	Time.	Change in press., mm.	Time.	Change in press., mm.	Change in press., mm.
0' 0"	0	11' 15"	60	47' 38"	121	374' 0"	146.5	
1 10	10	18 31	80	66 0	131	570 0	146.5	
2 39	20	28 29	100	129 0	142	—	—	
6 19	40	40 23	115	264 0	145.5	—	—	

The first stage of the decomposition gives an increase in pressure roughly equal to the original pressure of the formate: the second stage is much slower and continues until the total increase is about 4/3 times the initial pressure.

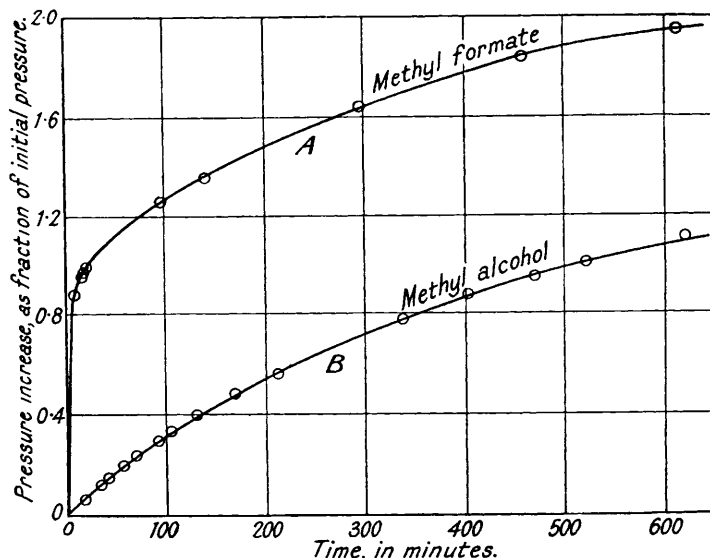
Analyses of the non-condensable reaction products were made at various stages towards the end of the reaction. The results were as follows : *

	Percentage after various times.				Percentage after various times.		
	1½ hrs.	3½ hrs.	6½ hrs.		1½ hrs.	3½ hrs.	6½ hrs.
CO ₂	20.3	15.4	13.7	CH ₄	27.8	29.3	29.8
CO	47.5	47.6	48.3	H ₂	4.4	7.7	8.2

* The figures given are corrected for the presence of decomposition products of the catalyst itself. In the preparation of samples for analysis, small quantities only of the catalyst were used, in order that the correction should be small. It was applied in the following way. In a typical analysis, the volume of gas remaining for combustion after removal of carbon monoxide and dioxide and unsaturated compounds was 155. Combustion gave: contraction 292, carbon dioxide formed 128, oxygen used 265. *iso*Propyl iodide decomposes according to the equation $2\text{C}_3\text{H}_7\text{I} = \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6 + \text{I}_2$. In the earlier stage of the analysis a volume 4 of unsaturated compounds had been found. This was all attributed to the propylene from the catalyst. Thus there would be 4 of propane in the saturated hydrocarbons burnt at the end; 4 of propane would give 12 of carbon dioxide, a contraction of 12, and an oxygen consumption of 20. Subtracting these from the corresponding figures given above, we obtain: gas

The high proportion of carbon monoxide in these analyses indicates that (b) is the principal mode of decomposition. Other significant facts are the lack of correspondence, in the later stages, between the amounts of methane and carbon dioxide, the decreasing proportion of carbon dioxide as time goes on, and the increasing amount of hydrogen. Much more methane is produced than can be accounted for by the reaction $\text{H}\cdot\text{CO}_2\text{CH}_3 = \text{CO}_2 + \text{CH}_4$. It is derived from the catalytic decomposition of the methyl alcohol formed in reaction (b). Further light is thrown on the matter at this point by an investigation of the uncatalysed reaction of the formate.

In the latter the intermediate formation of methyl alcohol can be clearly demonstrated. At 550° the two stages of the reaction are rather sharply separated as shown in the fig.:



a rapid increase in pressure to about double the initial value is followed by a very much slower increase due to the further decomposition of the intermediate product. Analysis of samples withdrawn as nearly as could be judged at the end of the initial rapid reaction showed the non-condensable product to consist principally of carbon monoxide, two examples of the percentages found being 71.6% and 78.5% respectively.

Since $\text{H}\cdot\text{CO}_2\text{CH}_3 - \text{CO} = \text{CH}_3\cdot\text{OH}$, it appears very probable that methyl alcohol is the other substance formed, and that reaction (b) is the predominant mode of decomposition. No formaldehyde could be detected by Schryver's test. The presence of methyl alcohol was proved by a quantitative comparison of the second part of curve A with the corresponding curve for the decomposition of pure methyl alcohol. The almost exact coincidence of B with the second part of A leaves no doubt about the identification.

Analysis of the products formed in the later stages of the decomposition in the absence of iodine shows a large increase in the proportion of hydrogen, as would be expected if the methyl alcohol decomposes according to the equation $\text{CH}_3\cdot\text{OH} = \text{CO} + 2\text{H}_2$. Thus at 552° , without iodine, the percentage of hydrogen in the non-condensable products formed after 3 hours was 21.0, that of carbon monoxide being 58.0, while after 6 hours the corresponding values were 30.8 and 54.0 respectively.

That methyl alcohol alone under similar conditions at 552° gives only carbon monoxide and hydrogen was confirmed by direct experiment, two samples yielding the results: CO, 32.8, 34.6; H_2 , 67.2, 65.4% respectively.

volume 151, contraction 280, carbon dioxide 116, oxygen used 245. The presence of ethane is very improbable. Thus we infer $\text{CH}_4 = 116$, $\text{H}_2 = 2/3 \cdot (280 - 232) = 32$. On this basis the calculated gas volume is 148 compared with the actual 151, while the calculated oxygen consumption is 248 compared with the 245 measured.

Thus the 100 mm. give a total pressure of 252 mm., *i.e.*, an increase of 1.52 times the initial pressure. The increase actually found when the decomposition had entirely ceased was 367 for an initial pressure of 252 mm., *i.e.*, 1.46 times.

Omitting the water, the composition of the non-condensable products can now be calculated and compared with those actually formed, the latter being in parentheses: CO₂, 13.8 (13.7); CO, 48.7 (48.3); CH₄, 34.3 (29.8); H₂, 3.2 (8.2)%. In the actual experiment the reduction of the methyl alcohol does not appear to have proceeded quite as far as would be anticipated from its behaviour alone. In other respects, all the facts seem to be adequately accounted for by the mechanism proposed.

The kinetics of the decomposition are naturally rather complex. With ethers and with acetaldehyde the catalytic reaction takes place at a rate directly proportional to the iodine concentration, and, for a given iodine concentration, the whole change is of the first order. The situation with methyl formate is complicated by the separation of the reaction into two stages, of which the second is the slower, and still more by the action of the hydrogen in converting some of the iodine into hydrogen iodide. The amount of iodine available for catalysing the primary decomposition is thereby lessened, but, on the other hand, the hydrogen iodide itself reacts with methyl alcohol, and so accelerates the second stage. For a given iodine pressure, the greater the concentration of the formate the larger will be the amount of hydrogen present at a given moment: thus the greater will be the amount of iodine removed. Hence the time required to reach a given stage of the reaction should increase as the initial pressure of the formate becomes greater. This expectation is fulfilled, as the following figures show: p is the initial pressure of the formate, and $t_{\frac{1}{3}}$ is the time required for one-third of the total pressure change to take place. The pressure of catalyst is 20 mm., and the temperature 451°.

p , mm.	51	113	156	228	301.5
$t_{\frac{1}{3}}$, secs.	202	249	302	360	400

In these figures the fact that the "end point" of the reaction varies somewhat with the initial concentration is allowed for.

The reaction between methyl alcohol and hydrogen iodide, which is an important step in the catalysis of the second stage of the decomposition, will presumably take place at a rate proportional to the hydrogen iodide concentration. If equilibrium in the system $H_2 + I_2 \rightleftharpoons 2HI$ were maintained, [HI] would be proportional to the square root of the iodine concentration. In so far, therefore, as the contribution of this reaction to the total change is important, it will reduce the proportionality between rate and catalyst concentration to a power less than unity. This also is confirmed by experiment: c was the concentration of catalyst, and the initial pressure of formate was approximately 100 mm., the temperature being 451°.

c , mm.	11	16.5	21.5	33.5	46.5
$t_{\frac{1}{3}}$, secs.	390	292	262	204	180

It was not considered profitable to attempt a more detailed analysis of the rather involved kinetic relationships thus revealed. All the observations are, however, qualitatively in agreement with theoretical expectations.

The uncatalysed decomposition of the formate is predominantly heterogeneous; but the reaction catalysed by iodine is mainly, if not entirely homogeneous. The rate of reaction of the formate was very much greater in a packed bulb, but on addition of iodine the rates in the packed and in the unpacked bulb approached one another closely.

Concn. of catalyst	0	10	23	41
Ratio of rates (Packed bulb)/(Unpacked bulb)	67	3.8	3.3	2.4

Methyl Alcohol.—Experiments were made on the catalysed decomposition of methyl alcohol itself. The mechanism of this reaction has already been explained. At 451° the ratio of the rate of decomposition with 14 mm. of catalyst to that with none was 6.4. For each molecule of methyl alcohol decomposing according to the equation $CH_3 \cdot OH = CO + 2H_2$, it is possible to have 4HI formed as a maximum. If these reacted immedi-

ately with two more molecules of methyl alcohol to give methane, with regeneration of iodine, the net result would be that the primary reaction rate would be multiplied by three. Thus on purely chemical grounds we can explain away a three-fold increase in rate, and this would only leave a factor of two for the influence of the iodine on the primary reaction. The methane formation is by no means complete, however, so that the factor must lie somewhere between two and six. It is, in any case, not very large.

The proportion of methane to hydrogen diminishes as the temperature increases :

Temp.	450°.	550°.	650°.
CO, %	38.3	37.0	33.5
CH ₄ , %	53.3	37.0	13.2
H ₂ , %	8.5	26.0	53.3

The *initial* rate of reaction is proportional to the iodine concentration, but the curves showing amount of decomposition against time show marked changes in direction near the beginning, due to the removal of catalyst by reaction with hydrogen. Unlike the catalysed reaction of the formate, that of the methyl alcohol appeared to be influenced to a great extent by the surface.

In general, the methyl alcohol decomposition is influenced by iodine to a much smaller extent than, and in a quite different way from, that of the ethers, aldehydes, and esters.

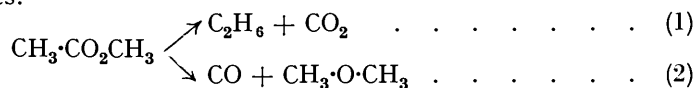
Acetic Acid and Methyl Acetate.—The acetic acid was purified by freezing and remelting fractions five times. At 550° its initial rate of decomposition is not appreciably influenced by iodine, but the later stages are affected :

Fraction decomposed	0.1	0.2	0.3	0.4	0.5	0.6
Time with I ₂ , secs.	23	50	81	128	183	267
Time without I ₂ , secs.	23	51	96	159	308	900

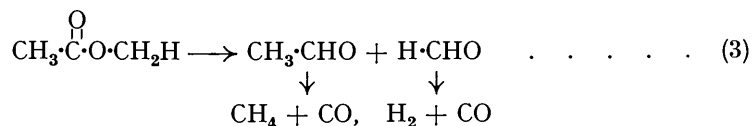
It seems reasonable to assume that the iodine does not catalyse the reaction in which we are interested, *viz.*, the primary decomposition of the acetic acid.

In a packed bulb the behaviour is complicated by condensation reactions, but the results show that the decomposition is by no means entirely heterogeneous.

Experiments were next made with a carefully dried and fractionated specimen of methyl acetate. If this ester decomposed in a manner similar to formic acid, it would yield the following products:



the ether decomposing further into methane, hydrogen, and carbon monoxide. Methyl acetate, however, contains the grouping C—O—C, and might decompose like an ether, giving acetaldehyde and formaldehyde :



This last mode of reaction has been found to predominate in the gaseous decomposition at about 500°. It is mainly homogeneous, and is strongly catalysed by iodine.

Temperature, 480°; initial pressure of ester, 130 mm.				
Catalyst, mm.	15	25.5	42	51.5
(Rate with catalyst)/(rate without catalyst)	34	45	69	81

Temperature, 500°; initial pressure of acetate, 130 mm.				
Fraction decomposed	0.2	0.3	0.4	
Time in packed bulb	10' 0"	17' 30"	26' 10"	
Time in unpacked bulb	11' 50"	18' 10"	24' 30"	

The influence of iodine in the packed bulb is the same as in the unpacked.

Analysis of the gaseous decomposition products showed the presence of 2% of carbon dioxide. This was assumed to come from reaction (1), and therefore to be accompanied by

an equal volume of ethane. The figures for methane and hydrogen given below have been corrected on the assumption that this ethane was really present, and give the relative proportions of the gases other than carbon dioxide and ethane.

Products of decomposition without iodine at 500°.

	(1.)	(2.)	(2) uncorr. for assumed C ₂ H ₄ .
CO, %	52.7	53.2	51.3
CH ₄ , %	29.7	28.6	33.6
H ₂ , %	17.6	18.2	15.1

Products of decomposition in presence of iodine.

CO, 54.7; CH₄, 33.2; H₂, 12.1%.

The latter figures are corrected for the presence of the small amounts of hydrocarbon derived from the catalyst itself.

Reactions (2) and (3) would both lead ultimately to the production of carbon monoxide, methane, and hydrogen in the proportions 2CO : CH₄ : H₂. The dimethyl ether formed in (2) gives formaldehyde as an intermediate product of its own decomposition. Thus, to establish mechanism (3) it is necessary to prove the intermediate formation of an aldehyde other than formaldehyde. It was possible to do this as follows. Gas samples were withdrawn from the reaction vessel about half-way through the decomposition, and dissolved in water. The solution gave a dense silver mirror with ammoniacal silver nitrate, but no trace of formaldehyde could be detected by Schryver's test. Blank tests showed that acetaldehyde neither gives this test itself nor interferes with the detection of formaldehyde. Mechanism (3) seems therefore to be the predominant one,* but the formaldehyde is decomposed or otherwise removed as fast as it is formed, none being detectable either at 550° or at 516°. In presence of iodine the amount of acetaldehyde accumulating is only enough to give a faint silver mirror : this is in accordance with the known marked catalysis by iodine of the acetaldehyde decomposition.

The total increase of pressure should be three times the initial pressure of the methyl acetate. In practice it varied from 1.93 to 2.03 times. Moreover, it will be noticed that the amount of hydrogen is too small, and that the ratio of carbon monoxide to methane is less than 2 : 1, as equation (3) would suggest. These discrepancies can be accounted for by assuming that some of the formaldehyde condenses with methyl acetate, and that the condensation product is reduced by the hydrogen of a second molecule of formaldehyde. If this type of condensation is assumed to occur to the extent necessary to account for the difference between the observed and the theoretical ratio CO/CH₄, then it can easily be calculated that the pressure increase during the whole reaction will correspond approximately to that actually observed.

The kinetics of the reaction are hardly suitable for elaborate investigation, since the hydrogen formed removes some of the catalyst, and the amount removed at any stage is a function of the velocity and equilibrium in the system H₂ + I₂ ⇌ 2HI. In presence of iodine, the accumulation of the intermediate products seems to be very small. Thus the rate of reaction is that of the initial decomposition of the ester, and is fairly accurately indicated by the rate of pressure change. At 523° the change, for a given catalyst concentration, is more nearly of the first than of any other order, but the values of *k* fall considerably as the reaction proceeds. At lower temperatures the fall is still more marked.

		Temperature 523°.						
Fraction decomposed	0.083	0.165	0.248	0.331	0.414	0.496	0.579
<i>k</i> × 10 ⁵	190	184	178	173	167	160	156
		Temperature 442°.						
Fraction decomposed	0.038	0.153	0.227	0.303	0.379	0.455	0.530
<i>k</i> × 10 ⁶	333	270	238	222	209	199	195

The fall can be explained by the progressive removal of iodine by the hydrogen.

* It can also be shown that methyl ether, if formed, would not decompose fast enough to account for the observed rate.

If the initial pressure of the acetate is increased, the absolute amount of hydrogen corresponding to a given fraction decomposed is greater, and thus a more serious removal of catalyst occurs. This means that for a given catalyst concentration the time required to reach a given stage of the decomposition will be greater the greater the initial pressure of acetate.

Temperature, 480°; catalyst, 20 mm.			
Initial press. of acetate, mm.	48	130·5	270
Time for 25% change, secs.	140	228	220

The disturbing influence of the hydrogen can be allowed for approximately as follows. From curves we can read off the times required for given absolute increases in pressure. Over these intervals, the hydrogen concentration, and therefore the catalyst concentration, can be regarded as the same for all initial pressures of acetate. Therefore, if the reaction is of the first order with respect to the acetate, $[1/(a-x)] \cdot \Delta p/\Delta t$ should be independent of the initial pressure. For example, the time required for the pressure increase to change from 10 to 20 mm. was 67 seconds at 480°, the initial pressure of acetate being 48 mm. The total pressure increase at the end of the reaction was 92·6 mm. Therefore the average amount of acetate present during the interval was proportional to $48(92·6 - 15)/92·6 = (a-x) = 40$. When the initial pressure was 130·5, the time for the increase to change from 10 to 20 mm. was 21 seconds, and the end-point was 252. Thus $(a-x)$ is $130·5(252 - 15)/252 = 123$. The product of the two times and their respective $(a-x)$ values should be independent of the initial pressure. The extent to which this is fulfilled is shown below:

Initial press., mm.	$(a-x)$.	Δt_{10-20} .	$(a-x) \times$ Δt_{10-20} .	$(a-x)$.	Δt_{20-30} .	$(a-x) \times$ Δt_{20-30} .	$(a-x)$.	Δt_{30-35} .	$(a-x) \times$ Δt_{30-35} .
48	40	67	268	35·1	85	298	31·7	52	165
130·5	123	21	259	118	24	283	114	13	148
270	263	12	316	257	12·5	321	253	6·5	164
		Mean	281		Mean	301		2 × Mean	318

For each range, Δp being constant, $(a-x)\Delta t$ is seen to be roughly constant. As we pass from the earlier to the later stages of the reaction, the mean value of $(a-x)\Delta t$ for a given Δp increases, corresponding to the fall in rate as the catalyst is removed.

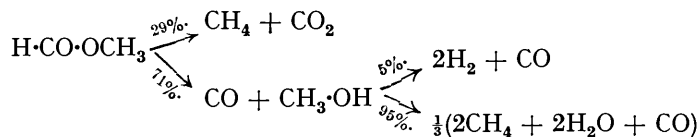
The Ethyl Halides.—The decomposition of the halides themselves is homogeneous. Iodine has no appreciable catalytic influence on the rate of the primary decomposition, though it alters the total pressure increase slightly.

Acetone and Methyl Ethyl Ketone.—Here also the results were negative, except for some disturbance of the later stages of the acetone reaction.

SUMMARY.

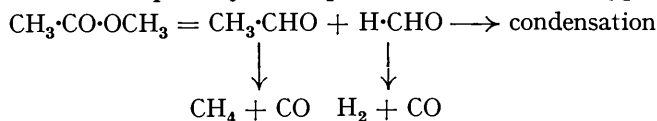
Iodine has a very pronounced catalytic influence on the homogeneous decomposition of methyl formate and methyl acetate in the gaseous state. The reactions are analogous to those of ethers and aldehydes. The decomposition of the corresponding acids is not catalysed.

The mode of decomposition of methyl formate in presence of iodine at 451° is as follows:



The predominant reaction is analogous to the catalytic decomposition of acetaldehyde, while the subsidiary reaction can be interpreted by regarding the methyl formate as an ether.

With methyl acetate the primary decomposition is of the ether type:



There is no marked catalysis by iodine of the decomposition of the ethyl halides, or of the ketones.

Methyl alcohol normally decomposes according to the equation $\text{CH}_3\cdot\text{OH} = 2\text{H}_2 + \text{CO}$, but in the presence of iodine the following reactions occur: (1) $\text{CH}_3\cdot\text{OH} = 2\text{H}_2 + \text{CO}$; (2) $\text{H}_2 + \text{I}_2 = 2\text{HI}$; (3) $\text{CH}_3\cdot\text{OH} + 2\text{HI} = \text{CH}_4 + \text{H}_2\text{O} + \text{I}_2$. Acceleration of the primary reaction does not exceed a factor of about three.

The kinetics of the various catalytic reactions are obviously rather complicated, but are found to resemble in a general way those of the simpler ether and aldehyde decompositions.

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