

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

## The Thermal Decomposition of Acetone Catalyzed by Iodine

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In a previous communication<sup>2</sup> it was reported that small amounts of iodine catalyze the decomposition of acetone. Although Hinshelwood and co-workers discovered and first studied<sup>3</sup> the iodine catalysis of the thermal decompositions of various organic compounds, Bairstow and Hinshelwood<sup>3c</sup> reported that iodine had no effect upon the decomposition of acetone. It is to be noted that in their investigations iodine was usually introduced by decomposing a sample of isopropyl iodide in the reaction vessel prior to the addition of the compound being studied. In a re-investigation of some of these decompositions, Faull and Rollefson<sup>4</sup> took absorption spectrograms of the reaction mixture during an experiment. They found that in almost every case iodine disappeared for some time during the course of the reaction, thereby demonstrating that a chemical mechanism is involved in the action of iodine.

In the present work the decomposition of acetone catalyzed by iodine has been studied and the products analyzed. Since compounds such as nitric oxide,<sup>5,7</sup> propylene,<sup>6,7</sup> and ethylene,<sup>8</sup> have been found to act as inhibitors in chain reactions, observations with regard to their influence upon the iodine catalyzed decomposition of acetone have been made.

Earlier work indicated that methyl iodide<sup>9</sup> and ethyl iodide, as well as the decomposition products of ethyl iodide, did accelerate the decomposition of acetone even though presumably isopropyl iodide had no effect.<sup>3c</sup> Therefore, the catalytic effects of methyl iodide, ethyl iodide, isopropyl iodide, and iodine were compared under similar experimental conditions. The effect of isopropyl iodide, which itself decomposes into propylene,

propane, and iodine,<sup>10</sup> was of particular interest because its use as a source of iodine results in the introduction of propylene into the reaction mixture. Under such conditions the catalytic effect of iodine might be altered by the inhibiting effect of propylene.

## Experimental

**Apparatus and Method.**—The furnace for maintaining the cylindrical Pyrex reaction vessel, 75 × 130 mm., at the elevated temperature was a slightly modified design of a type previously used.<sup>11</sup> Adjacent to the reaction vessel and surrounded by the same graphite cylinder was another bulb filled with nitrogen and connected to an external manometer. With the tungsten contact of the manometer connected to a vacuum tube relay circuit, an additional heating current was automatically cut on or off so as to maintain a constant temperature to within  $\pm 0.5^\circ$ . The temperature at the center of the reaction vessel was measured by the use of a chromel-alumel thermocouple connected to a potentiometer circuit. New thermocouples previously standardized at the sulfur boiling point were used frequently so that the temperature measurements should be accurate to within  $\pm 1^\circ$ .

Iodine was introduced into the reaction vessel by means of an all-glass valve of the type described by Willard<sup>12</sup> with the modification that an inner capillary of Nonex glass was used to facilitate opening and sealing off. After the addition of the iodine vapor, acetone vapor was allowed to flow into the reaction vessel through a Bodenstein valve with a silver chloride seat, as designed by Kistiakowsky. All external capillary tubing and valves were heated by wrapping with resistance wire. The pressure measurements were made with a click gage together with either a mercury manometer or, for low pressures, an  $\alpha$ -bromonaphthalene manometer. The remainder of the system, consisting of supply bulbs, mixing bulbs, traps, etc., suitable for the introduction and removal of materials from the reaction vessel, was connected to a diffusion pump to allow evacuation of the entire system to  $10^{-2}$ – $10^{-4}$  mm. before each run. In some runs the Bodenstein valve was replaced either by a Christ valve<sup>13</sup> or by a heated "No-lube" stopcock greased with a small amount of polybutene. Within the limits of experimental error no difference in the results with the various types of valves, or stopcock, was observed.

The method for introducing a pressure of a compound greater than its vapor pressure at room temperature was similar to that already described.<sup>14</sup> For the gas analyses the products were expanded through a dry-ice trap into an evacuated two-liter bulb, from which a sample could be removed by use of a Toepler pump. The analyses for acidic

(1) Fellow of the Sherman Clarke Fund for Chemical Research, University of Rochester.

(2) Gantz and Walters, *THIS JOURNAL*, **62**, 996 (1940).

(3) Glass and Hinshelwood, *J. Chem. Soc.*, 1804 (1929); (b) Clusius and Hinshelwood, *Proc. Roy. Soc. (London)*, **128A**, 82 (1930); (c) Bairstow and Hinshelwood, *ibid.*, **142A**, 77 (1933); *J. Chem. Soc.*, 1147 (1933).

(4) Faull and Rollefson, *THIS JOURNAL*, **58**, 1755 (1936); **59**, 625 (1937).

(5) Staveley and Hinshelwood, *Proc. Roy. Soc. (London)*, **159A**, 192 (1937).

(6) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938).

(7) Echols and Pease, *THIS JOURNAL*, **61**, 1024 (1939).

(8) Fletcher and Rollefson, *ibid.*, **58**, 2129, 2135 (1936); Staveley, *Proc. Roy. Soc. (London)*, **162A**, 557 (1937).

(9) Rice, Leatherman and Weiler, unpublished results.

(10) Jones and Ogg, *THIS JOURNAL*, **59**, 1939 (1937).

(11) Rice and Walters, *J. Chem. Phys.*, **7**, 1015 (1939).

(12) Willard, *THIS JOURNAL*, **57**, 2328 (1935).

(13) Christ and Brown, *Ind. Eng. Chem., Anal. Ed.*, **11**, 396 (1939).

(14) Walters, *THIS JOURNAL*, **62**, 880 (1940).

material, such as ketene or hydrogen iodide, were carried out as in a previous investigation<sup>14</sup> with precautions to eliminate any errors due to carbon dioxide. To obtain a pressure of iodine lower than could be read with accuracy on the  $\alpha$ -bromonaphthalene manometer, a measurable amount of iodine together with a known pressure of nitrogen was allowed to mix thoroughly in the reaction vessel. The larger part of the mixture was then removed and the pressure remaining in the bulb measured. Of the few mm. of gas mixture remaining only a very small amount of iodine was present. It was found that the small amount of nitrogen had no influence on the rate, and the accuracy of the method for obtaining low pressures of iodine was proved by analyzing for the iodine left in the bulb.

The gas analyses were performed in a modified constant volume apparatus,<sup>15</sup> in which a 5-cc. sample could be analyzed with an accuracy of  $\pm 0.5\%$ . Reagents consisting of potassium hydroxide, alkaline pyrogallol, and activated sulfuric acid were contained over mercury in small absorption pipets. Hydrogen and carbon monoxide were oxidized over copper oxide and the hydrocarbons were burned with oxygen over a heated platinum wire.

**Materials.**—Merck reagent acetone was dried over calcium sulfate and fractionated twice before use. The middle fraction with a boiling range of  $0.1^\circ$  or less had a boiling point of  $56.3^\circ$ . Merck reagent resublimed iodine was thoroughly evacuated before use. Biacetyl was purified as in a previous study.<sup>14</sup> Dioxane was purified according to the method of Scatchard and Benedict.<sup>16</sup> Tetrahydrofuran was prepared by the hydrogenation of furan at  $90^\circ$  under 700 pounds pressure. Ethyl methyl ketone and diethyl ketone were treated with ferrous sulfate to remove peroxides. Isopropyl iodide was shaken with mercury to remove free iodine. All the liquids used in the work, including those above, were Eastman Kodak Co. best grade, unless otherwise indicated, and they were dried over calcium sulfate and fractionated before use. Ethylene and propylene, obtained from the Ohio Chemical Co., had stated purities of 99.5%. Nitric oxide was prepared by the method of Johnston and Giaque.<sup>17</sup> Ketene was prepared according to the procedure of Rice.<sup>18</sup>

**Spectroscopic Observations.**—These experiments were made using a Pyrex reaction vessel,  $75 \times 140$  mm., on each end of which was a one inch plane window. The furnace, the temperature of which was manually controlled to within  $1^\circ$ , was similar to the one employed in the ordinary runs except for changes to allow passage of a light beam through the vessel and onto the slit of a spectrograph. Light from a fifty candle-power lamp, collimated by a lens, passed through a blackened copper screen to reduce the intensity and through a Wratten filter no. 78a to obtain a more uniform intensity distribution on the photographic plate. A Bausch and Lomb large spectrometer with camera attachment was used together with Eastman spectroscopic plates. Type 103-C plates proved the most satisfactory.

The spectroscopic observations for experiments in the neighborhood of  $492^\circ$  with iodine pressures exceeding 3.3

mm. and acetone pressures near 200 mm. demonstrated that some molecular iodine did exist at all times during the reaction. For a number of runs with iodine pressure in the range 3.3 to 21 mm., the iodine spectrum could be readily observed in the exposures made at various time intervals during the reaction. With high initial iodine pressures the considerable absorption indicated that large amounts were always present, but with lower pressures the iodine bands became rather weak about two minutes after acetone had been added. Therefore, photographs were taken for runs with iodine pressures from 2.6 mm. down to 0.8 mm. In these experiments the iodine always completely disappeared for at least a short interval. The interval of practically complete disappearance usually fell within the period two to three minutes after the acetone had been added. Only relatively small amounts of iodine, if any, were present in the period one to four minutes. Apparently the major portion of the iodine returns after six to eight minutes. In Fig. 1 are shown the densitometer tracings for exposures during a run. The periodic variation in density, which is indicative of the presence of the iodine bands disappears and then reappears. The tracing after 2.0 minutes is almost identical with that of the source.

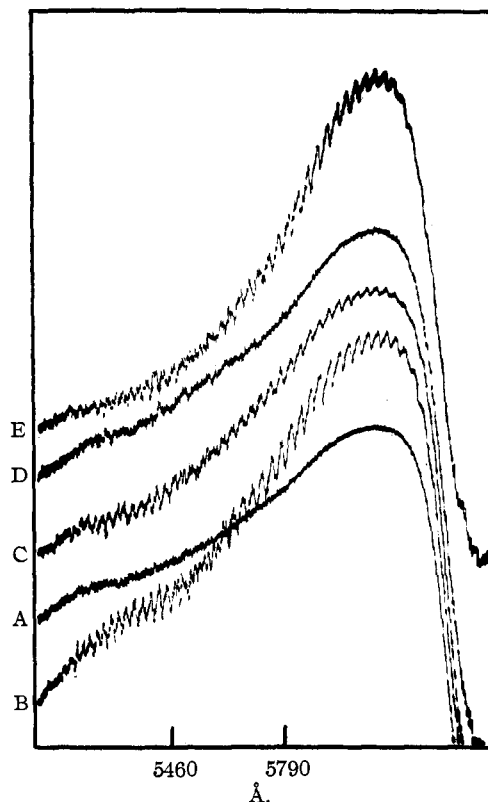


Fig. 1.—Densitometer tracings of exposures made during an experiment with 200 mm. acetone and 2.06 mm. iodine at  $493^\circ$ : A, source; B, iodine; C, D, E, exposures started 0.5, 2.0 and 6.0 minutes after acetone was added; exposure time, 0.1 minute; except for E, 0.2 minute. For clarity, tracings are slightly displaced.

However, a quantitative measure of the iodine present during the reaction could not be obtained, because, as the

(15) The apparatus was similar to that of Ambler, *Analyst*, **54**, 517 (1929).

(16) Scatchard and Benedict, *THIS JOURNAL*, **58**, 837 (1936).

(17) Johnston and Giaque, *ibid.*, **51**, 3194 (1929).

(18) Rice, Greenberg, Waters and Vollrath, *ibid.*, **56**, 1760 (1934).

decomposition occurs, the intensity of the light passing through the reaction vessel is reduced by the gradual formation of a deposit on the inner walls. With smaller amounts of iodine, the iodine disappeared for a somewhat longer time. In order to determine how small an amount of iodine could have been present and escaped detection, photographs of decreasing amounts of iodine in the presence of 200 mm. of nitrogen were made. It was found that bands were clearly visible with an iodine pressure of 0.12 mm. and at a pressure of 0.06 mm. only a few bands could be seen. Although no difference in the rate was observed under the usual conditions with the light on or off, a 500-watt projection lamp was used as a light source for runs at 457° with 4.4 and 17 mm. of iodine in order to determine whether the reaction was photosensitive. Under these conditions the light had no noticeable effect. Figures 2 and 3 were made during runs with iodine and biacetyl and with iodine and dioxane, respectively. However, these will be discussed later.

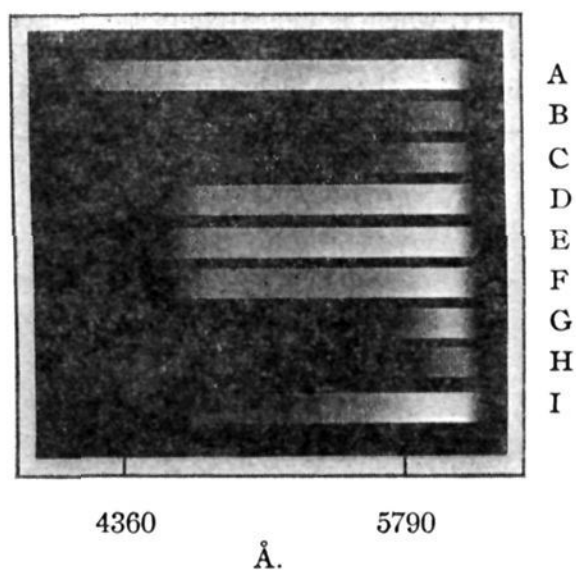


Fig. 2.—Biacetyl, 197 mm., with 12 mm. of iodine at 421°: A and I, source before and after experiment; B, iodine; C, D, E, F, G, H, exposures started 0.1, 1, 5, 30, 90, 120 minutes after biacetyl was added; exposure times: A, B, C, D, 0.3; E, 0.45; F, 2.25; G, 6; H, I, 10 minutes.

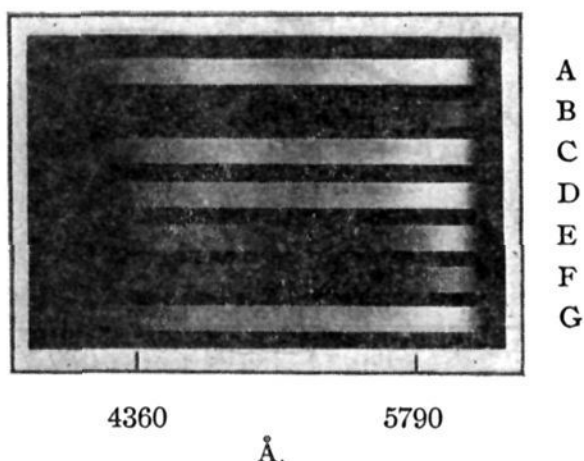


Fig. 3.—Dioxane, 154 mm., and 10.9 mm. of iodine at 448°: A and G, source before and after the experiment; B, iodine; C, D, E, F, exposures started 0.1, 10, 30, 60 minutes after dioxane was added; exposure time, 0.25 minutes.

**Effect of Surface.**—In Table I are summarized the experiments carried out to determine the homogeneity of the

iodine catalyzed acetone decomposition. Thin-walled Pyrex tubes packed into the reaction vessel increased the surface to volume ratio thirty-five fold. The over-all pressure increase in the packed bulb, which was found to be 119% compared with 144% in the unpacked bulb, indicates that more condensation or polymerization occurs in the packed vessel.

TABLE I  
EFFECT OF SURFACE ON THE IODINE CATALYZED DECOMPOSITION OF ACETONE

Temp., °C.	Vessel	$P_A$ , <sup>c</sup> mm.	$P_{I_2}$ , mm.	$t_{1/4}$ , min.	$(dP/dt)_{1/4}$ , mm./min.
494	Packed <sup>a</sup>	214	2.6	239	0.54
494	Unpacked	211	2.8	27	2.1 <sup>b</sup>
492	Packed <sup>a</sup>	220	4.5	220	0.43
495	Unpacked	210	3.7	26	2.0

<sup>a</sup> In the packed vessel surface to volume ratio increased by a factor of thirty-five. <sup>b</sup> Average of two runs. <sup>c</sup>  $P_A$  denotes initial pressure of acetone.

The time necessary for one-quarter of the acetone to decompose,  $t_{1/4}$ , was considerably longer in the packed vessel. The rate in the packed vessel is slow at the start, but in the unpacked vessel the rate is fastest near the beginning. Nevertheless, even at one-quarter decomposition, where the rate in the packed vessel is not far from its maximum, the rate of pressure increase,  $(dP/dt)_{1/4}$ , is markedly slower in the packed vessel. These results indicate that the iodine catalysis is not a heterogeneous reaction. The slower rate with increased surface may be the result of chain breaking at the walls.

## Results and Discussion

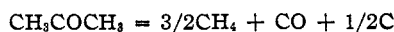
**Products of the Reaction.**—The ratio of the final pressure of the products to the initial acetone pressure was determined for acetone pressures in the range 180–220 mm. and iodine pressures of 2.7–5.3 mm. The average values of  $P_f/P_i$  at 494, 510 and 517° were 2.44, 2.46 and 2.43, respectively. With change in conditions this value underwent no appreciable variation. The results of the gas analyses, given in Table II, reveal that methane and carbon monoxide are the principal gaseous products. The material absorbed in the potassium hydroxide represents

TABLE II  
GASEOUS PRODUCTS AT 496°

$P_A$ , mm.	$P_{I_2}$ , mm.	% Dec.	Abs. KOH	Un-satd.	H <sub>2</sub>	CO (mole %)	CH <sub>4</sub> (%)	C <sub>2</sub> H <sub>6</sub>
207	4.7	7.5	0.8	1.9	0	38.5	57.8	0.8
224	3.9	28	.2	0.	0.2	38.3	59.4	2.0
213	25.6	52	.6	0.	0	39.0	60.6	0.4
204	4.1	56	.4	.4	0.4	38.0	60.9	0
209	3.6	77	.5	0	.1	38.3	61.2	0
212	3.9	95	.9	0.3	.4	37.5	61.0	0
208	3.6	100	1.1	0.2	0	37.4	60.6	0
200	0	25	3.1	10.1	1.4	29.4	54.5	0 <sup>a</sup>
200	0	98	4.7	8.0	2.1	42.0	42.4	1.5 <sup>a</sup>

<sup>a</sup> Analyses of Winkler and Hinshelwood for pure acetone at 602°.

carbon dioxide together with traces of ketene or hydrogen iodide. The analysis for the run with the high iodine pressure shows that a change in iodine pressure does not affect the nature of the products. Since the relative percentages of the products do not vary appreciably as the decomposition proceeds, it is not likely that any large quantities of intermediate compounds build up during the reaction. Comparison with the gaseous products obtained by Winkler and Hinshelwood<sup>19</sup> for acetone alone shows that in the iodine-catalyzed decomposition the percentage of unsaturates is smaller and the percentage of methane larger. Inspection of the vessel after several runs and, as already mentioned, observations made during the spectroscopic work showed that a considerable deposit, apparently carbon, formed on the walls of the vessel. It was also observed that there were no significant amounts of products (less than 3%) which were volatile at the elevated temperature, but condensable at  $-80^{\circ}$  under a pressure of 20 mm. All these facts indicate that the over-all reaction is



Since ketene might be present in the iodine-catalyzed reaction, just as in the ordinary decomposition<sup>19,20</sup> and since in the presence of iodine hydrogen iodide might be present also, determinations were made for acidic substances other than carbon dioxide. For experiments in the temperature range  $469\text{--}517^{\circ}$  with acetone pressures near 200 mm. and iodine pressures from 1.3 to 4.9 mm., the maximum amount of acidic material titrated would correspond to only 0.8 mm. of gas at the temperature of the reaction vessel. With various amounts of decomposition from 5 to 66% the average amount of acidic material corresponded to 0.5 mm. Addition of silver nitrate to the material in water solution indicated only a trace of iodide ion. Therefore, the sum of the pressures of ketene and hydrogen iodide present at any time during the reaction would appear to be small.

**Rate Measurements.**—Two representative pressure-time curves, shown in Fig. 4, indicate that there is an initial rapid increase in pressure followed by a slower rate of pressure increase, which falls off very gradually until the reaction is nearing completion. During the portion of the reaction from about 20 to 80% decomposition,

(19) Winkler and Hinshelwood, *Proc. Roy. Soc. (London)*, **149A**, 340 (1935).

(20) Hurd and Tallyn, *THIS JOURNAL*, **47**, 1427 (1925); Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

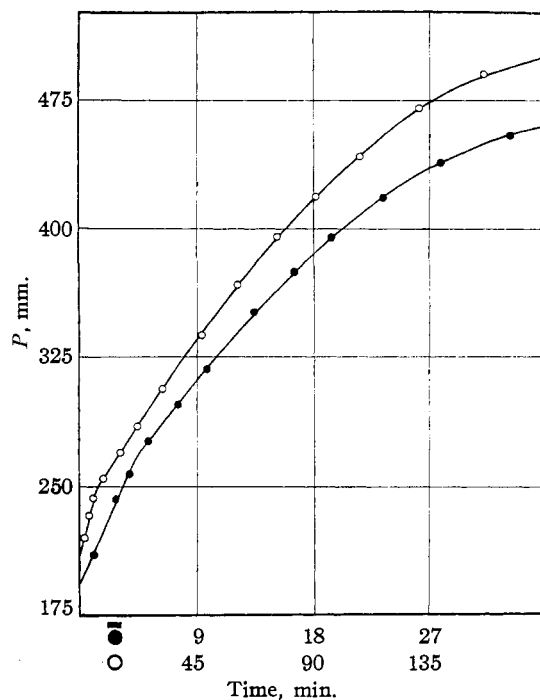


Fig. 4.—Decomposition of acetone in the presence of iodine: ●, 197 mm. acetone, 4.75 mm. iodine,  $517^{\circ}$ ; ○, 212 mm. acetone, 3.89 mm. iodine,  $496^{\circ}$ .

the rate varies approximately as the square root of the acetone pressure. In the neighborhood of  $496^{\circ}$  the transition from the initial fast rate to the slower rate occurs after a pressure increase of 15–20%. With increase in temperature the transition occurs at slightly greater decomposition. The maximum rate for the run at  $496^{\circ}$  in Fig. 4 is twenty times greater than that for pure acetone, and the rate after 25% pressure increase is about six times that of acetone alone. A comparison of the rate of decomposition at the point of 25% pressure increase for different runs at  $492^{\circ}$  with acetone pressure from 100–400 mm. and constant iodine pressure indicates that the rate is approximately proportional to the square root of the pressure of undecomposed acetone. However, since the variation with acetone pressure is not large, experimental errors are relatively important. The dependence of the initial fast rate upon the acetone pressure, which is about 0.7 order, is probably of less importance, because in this period the concentration of iodine may vary considerably.

With increase in iodine pressure the catalytic effect reaches a maximum, then decreases and levels off. At high iodine pressures the rate is almost independent of the iodine pressure. This

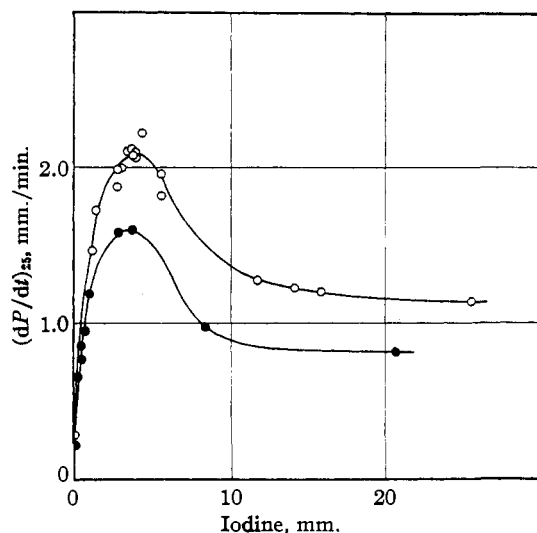


Fig. 5.—Variation of the rate of decomposition of 200 mm. of acetone with pressure of added iodine: ●, 492°; ○, 495°.

is shown in Fig. 5 in which the rate after 25% pressure increase,  $(dP/dt)_{25}$ , is given as a function of the iodine pressure. The iodine pressures are the total pressures, molecular iodine plus iodine atoms, which would be observed experimentally under conditions of equilibrium at the furnace temperature. Only runs within 1° of the temperature indicated and near 200 mm. of acetone pressure were chosen so that corrections for pressure and temperature differences were small. Plots of either the fast initial rate *vs.* iodine pressure or the reciprocal of the time for the pressure to increase 25% *vs.* iodine pressure give curves similar to those in Fig. 4. At the lower iodine pressure it appeared that the maximum rate near the beginning was not attained instantaneously<sup>21</sup> and at the higher pressures of iodine this was more noticeable. It did not seem to be a question of mixing, but, from the results of the spectroscopic experiments, it would appear that the maximum rate is attained only after part or all the iodine has disappeared.

In Table III are shown some of the runs at different temperatures. The iodine pressures were kept near 3–4 mm. since, in this range of iodine pressures, the catalytic effect is a maximum, and slight changes do not cause much variation in rate. The quantity  $(dP/dt)_m$  represents the maximum rate during the initial fast period and  $(dP/dt)_{25}$ , which was chosen so as to obtain a measure of the

(21) The complexities involved in the operation of the apparatus made it difficult to obtain more than one or two pressure readings during the first minute.

rate after the fast period for the higher temperatures, denotes the rate after 35% pressure increase. From these two quantities an approximate activation energy of 70 kcal. was obtained for the limited temperature range used. The activation energy calculated from the maximum rate was somewhat lower than that from the subsequent rate. For any quantitative comparisons,

TABLE III

DECOMPOSITION OF ACETONE IN THE PRESENCE OF IODINE

Temp., °C.	$P_A$ , mm.	$P_{I_2}$ , mm.	$(dP/dt)_m$ , mm./min.	$t_{25}$ , min.	$(dP/dt)_{25}$ , mm./min.
493	219	3.78	5.8	18.0	1.88
495	199	0	0.36	150	...
495	201	4.27	7.1	12.8	2.24
496	212	3.89	7.1	13.0	2.28
500	221	3.78	11	9.6	3.06
500	246	3.44	12	11.4	3.28
509	198	3.22	17	4.3	5.22
510	192	3.08	18	3.7	5.00
510	198	4.50	17	3.5	5.43
512	198	0	0.93	...	...
517	200	4.55	22	2.5	8.4
517	204	5.2	23	3.5	8.2

the time for 25% pressure increase,  $t_{25}$ , was of little value, since the amount of reaction occurring in the initial fast period varies with temperature. A few runs which were made near 470° were appreciably slower than the above activation energy would indicate. However, since neither over-all pressure measurements nor analyses of products have been made at 470°, it is possible that some change in the nature of the reaction occurs at the lower temperatures. On account of the complex nature of the reaction, further experiments are necessary to obtain an accurate activation energy.

Since many of the results suggested that the iodine catalyzed decomposition might involve a chain mechanism, the influence of various inhibitors was tried. Data from these experiments are given in Table IV, in which  $\Delta P_{20-0}$  represents the pressure increase after twenty minutes. Typical runs are shown in Fig. 6. Since any pressure decrease which either propylene or ethylene undergoes in the presence of iodine would make the apparent inhibition greater than the actual one, experiments were made with propylene and iodine, and with ethylene and iodine. At 494° in the presence of 3.7 mm. of iodine, 200 mm. of propylene underwent a pressure decrease of 9.1% in twenty minutes. Under similar conditions with 3.5 mm. of iodine the pressure decrease for 198 mm. of ethylene was 3.1%. From these re-

TABLE IV  
EFFECT OF VARIOUS SUBSTANCES UPON THE IODINE-CATALYZED DECOMPOSITION OF ACETONE

Temp., °C.	$P_A$ , mm.	$P_{C_2H_6}$ , mm.	$P_{I_2}$ , mm.	$\Delta P_{20-0}$ , mm.
494	191	0	3.88	58.9
495	173	17 <sup>a</sup>	3.58	3.5
494	150	14 <sup>a</sup>	3.09	2.6
$P_{C_2H_4}$				
495	184	77 <sup>a</sup>	2.83	7.6
495	212	11	4.55	18.1
493	206	0	3.34	55.4
$P_{NO}$				
495	201	11	3.33	15.5
494	148	5.2 <sup>a</sup>	3.50	9.8
494	208	0	3.61	43.6

<sup>a</sup> Iodine was introduced into the reaction vessel and then a mixture of acetone and inhibitor added. In all other runs iodine was introduced into the reaction vessel and then inhibitor added, followed by acetone.

sults it is evident that the maximum error at the lower pressures used in the runs in Table IV would not exceed 2-3 mm., even if the rate of pressure decrease is first order with respect to the pressure of unsaturate. A correction of this magnitude would not alter the data appreciably. With regard to the inhibition by nitric oxide it is apparent from Fig. 6 that, as has been observed previously,<sup>5,7</sup> the inhibition is only of transient nature.

The data from typical experiments with added alkyl iodide instead of pure iodine are summarized in Table V. The decomposition of the organic

TABLE V  
COMPARISON OF THE CATALYTIC EFFECTS OF IODINE AND ALKYL IODIDES

Temp., °C.	$P_A$ , mm.	$P_{I_2}$ , mm.	$\Delta P_{20-0}$ , mm.
492	146	3.0	44.0
495	205	5.3	59.0
496	201	2.7	62.3
$P_{CH_3I}$			
496	164	5.2	50.5
494	164	5.9	50.3
$P_{C_2H_5I}$			
492	174	3.8	19.9
492	168	15.9	11.7
$P_{i-C_3H_7I}$			
496	201	5.4	8.1
494	166	5.6	6.1
496	186	9.8	6.1 <sup>a</sup>
495	184	20.0	4.8 <sup>a</sup>
493	204	0	6.6
492	198	0	4.6

<sup>a</sup> Isopropyl iodide allowed to decompose in furnace before acetone was added. In all other runs mixtures of acetone and iodide, previously prepared, were used.

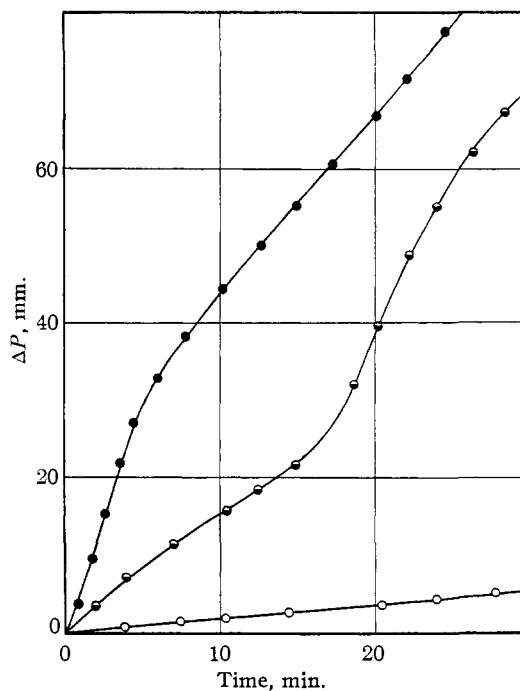


Fig. 6.—Effect of various substances upon the iodine catalyzed decomposition of acetone at 495°: ●, 201 mm. acetone, 4.27 mm. iodine; ●, 201 mm. acetone, 3.33 mm. iodine, 11 mm. nitric oxide; ○, 173 mm. acetone, 3.58 mm. iodine, 17 mm. propylene.

iodide results in the production of an iodine pressure one-half as large as the original iodide pressure. In the case of the majority of runs, in which mixtures of acetone and iodide were introduced into the furnace, the decomposition of the iodide itself, which at these temperatures should occur very rapidly, may provide free radicals in addition to supplying iodine. However, in the experiments with isopropyl iodide already decomposed in the furnace, the results were similar to those obtained with mixtures. This was also true for experiments with ethyl iodide. With isopropyl iodide the amount of decomposition is not markedly different from that of pure acetone. With increasing amounts of isopropyl iodide, the rate may decrease slightly. On the other hand for methyl iodide and acetone the pressure-time curves were quite similar to those of iodine and acetone. The slow rate in the presence of isopropyl iodide may be due to the presence of propylene and, in the case of ethyl iodide, to the presence of ethylene. Irrespective of the cause, it is evident that in one case, namely, acetone, isopropyl iodide is not a satisfactory source of iodine for the study of iodine catalysis. At present it is not known whether, in other investiga-

tions where isopropyl iodide has been used, the presence of propylene may have some disturbing influence.

The results of the present investigation indicate that the decomposition of acetone catalyzed by iodine is a complex reaction which involves the chemical reaction of iodine. Inhibition, particularly by nitric oxide, shows that radicals or atoms play an important role in the decomposition. Since nitric oxide does not react with iodine, the inhibition cannot be due to any removal or destruction of the iodine. It might be assumed that the decomposition is started by iodine atoms from the equilibrium



which react with acetone, probably resulting in the removal of a hydrogen atom. Estimations of the rates of various possible reactions, as well as the experimental observations, indicate that a simple bimolecular reaction between molecular iodine and acetone is less likely than reactions involving iodine atoms. If, in the presence of iodine, the remainder of the reactions occurred according to the Rice-Herzfeld mechanism<sup>22</sup> for the normal decomposition of acetone, ketene should appear as an intermediate. In the analyses of the gaseous products only a very small amount of ketene, some of which may come from the normal decomposition, was found. This result might be explained by assuming either the destruction of the ketene as the gases are removed from the furnace or the occurrence of a sufficiently rapid iodine catalyzed decomposition of ketene. An accelerated decomposition of ketene in the presence of iodine was actually observed. At 498° in the presence of 1 mm. of iodine about one-half of a 12-mm. sample of ketene decomposed during the first minute. With 108 mm. of ketene and 3.1 mm. of iodine more than half of the decomposition took place within one minute. Although the reaction was so fast that these results are only qualitative, the rate of decomposition does not seem to be quite sufficient to keep the ketene concentration so low. The analyses from the latter experiment were

Abs. KOH	Unsat.	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
1.7	9.3	0.7	66.9	20.5	0.7

The presence of unsaturates in the ketene decomposition and their almost complete absence in the acetone decomposition would appear to be

further evidence against ketene as an intermediate, unless the products from the decomposition of ketene in the presence of acetone are not the same as those from ketene alone. Moreover, the analytical results appear to rule out other possible intermediate compounds. In view of these facts, it does not seem appropriate to attempt to give a detailed mechanism at this time.

The cause of the reappearance of iodine after its initial disappearance is probably due to the building up of intermediate compounds or radicals which either slow down the rate of iodine consumption or aid its regeneration. If the reaction between an alkyl iodide and hydrogen iodide is responsible for the regeneration of iodine, then, as calculations from Ogg's rate equations<sup>23</sup> show, the simple bimolecular reaction is less important at 492° than the mechanism involving the dissociation of the alkyl iodide. The decrease in the catalytic effect with increase in iodine is probably due to the occurrence of the reaction



which reduces the concentration of radicals and thus slows down any reaction in which R is involved. It is, perhaps, of interest to note that at high iodine pressure, if (2) were an equilibrium reaction involving acetyl radicals and if acetyl iodide and hydrogen iodide were in equilibrium with acetone and iodine, it is possible to obtain a rate expression which depends upon the square root of the acetone pressure and is independent of the initial iodine pressure.

**Other Compounds.**—In view of the catalytic effect of iodine upon the acetone decomposition, a preliminary investigation of the influence of iodine on other ketones, as well as several other compounds, was made. A number of experiments were carried out for each substance, a few of which are given in Table VI. It had also been reported<sup>3c</sup> that iodine, presumably, decomposed isopropyl iodide, had no effect upon ethyl methyl ketone, but from the present work it is apparent that iodine does accelerate the decomposition. However, the iodine catalysis is less with ethyl methyl ketone than with acetone, and with diethyl ketone the effect is even smaller. In contrast to acetone, photographs of runs in the neighborhood of 486–512° with 200 mm. of ethyl methyl ketone and iodine pressures up to 14 mm., the iodine bands disappeared completely as soon as the ketone was added and stayed away for some

(22) Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).

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



TABLE VI  
EFFECT OF IODINE ON OTHER DECOMPOSITIONS

Compd.	Temp., °C.	$P_C$ , mm.	$P_{I_2}$ , mm.	$t_{1/2}$ , min.	$\Delta P_{I_2-0}$ , mm.
EtCOMe	486	194	0	...	6.6
EtCOMe	486	190	5.1	30.6	36.7
Et <sub>2</sub> CO	495	215	0	20.7	117
Et <sub>2</sub> CO	494	223	14.8	5.4	278
Ac <sub>2</sub>	422	145	0	...	9.8
Ac <sub>2</sub>	418	196	0	...	13.4 <sup>a</sup>
Ac <sub>2</sub>	421	197	12.0	24.4	81.8
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	451	180	0	...	3.0 <sup>b</sup>
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	449	147	9.9	3.9	189 <sup>b</sup>
C <sub>4</sub> H <sub>8</sub> O	451	182	0	...	1 <sup>b</sup>
C <sub>4</sub> H <sub>8</sub> O	447	205	9.5	2.4	201 <sup>b</sup>

<sup>a</sup> Run from previous study. <sup>b</sup>  $\Delta P_{I_2-0}$ . <sup>c</sup>  $P_C$  denotes initial pressure of compound.

time, during which a large part of the decomposition occurred. Similar results were obtained at 494° for diethyl ketone with 15 mm. of iodine, but with 30 mm., the major portion of the iodine disappeared, but not all of it. It was observed that the decomposition of biacetyl is also catalyzed by iodine, and during a run the dependence of the rate upon the biacetyl pressure was somewhat less than first order. As shown in Fig. 2, the iodine disappears and remains away until the decomposition is nearly complete.

In the case of all these ketones, a carbonaceous film, which was deposited on the walls, lowered the light intensity as the reaction proceeded.

The increase in rate on the addition of iodine to either dioxane or tetrahydrofuran was much greater than the effect observed with any of the ketones. The iodine disappears as soon as dioxane is added, as Fig. 3 illustrates, and returns only near the end of the reaction. The work with tetrahydrofuran was undertaken in connection with the study of the normal decomposition which is being investigated in this Laboratory, and it was found that iodine added to this compound behaved as with dioxane except that not all of the iodine had returned even near completion. It has been reported that iodine catalyzes the decomposition of cyclohexane.<sup>24</sup> Although no kinetic measurements were made, it was found that near 490° the iodine disappeared when 200 mm. of cyclohexane was added to 10 mm. of iodine. In

(24) Berents and Frost, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 883 (1939).

agreement with the work of Faull and Rollefson<sup>4</sup> on other substances, the present results indicate that in general the iodine catalysis involves a chemical reaction.

However, in the case of diethylamine, they reported that iodine does not disappear. Although their exact experimental conditions were not given, it seemed possible that, as with acetone, small amounts of iodine might disappear even though large amounts did not. Therefore, a few runs were made in the region 400–450° with 90–200 mm. of diethylamine and 3–16 mm. of iodine. Under these conditions it was found that the larger amounts of iodine, as well as the smaller amounts, completely disappeared as soon as the diethylamine was added and did not return even after one or more hours.

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### Summary

The homogeneous decomposition of acetone catalyzed by iodine has been studied in the region 470–517°. The analyses of the products, together with the measurements of the pressure increase, indicate that the overall reaction is:  $\text{CH}_3\text{COCH}_3 = \frac{3}{2}\text{CH}_4 + \text{CO} + \frac{1}{2}\text{C}$ . With increasing pressures of iodine the catalytic effect reaches a maximum and then decreases to an almost constant value. The catalyzed decomposition is markedly retarded by the addition of nitric oxide, propylene or ethylene. Spectroscopic observations showed that, with low pressures of iodine, the iodine disappears for a short time during the decomposition. The effect of methyl iodide on the acetone decomposition was comparable to that of iodine, ethyl iodide was less effective, and isopropyl iodide had practically no effect.

Iodine was found to catalyze the decompositions of ethyl methyl ketone, diethyl ketone, biacetyl, dioxane, and tetrahydrofuran. In every case the iodine disappeared during a period in which a large part of the decomposition occurred.

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