tion of ligroin; m. p. $155-156^{\circ}$; spec. rot. $-38^{\circ} \longrightarrow +15^{\circ} (25^{\circ}; c, 5; abs. CHCl_{3}, 24 hrs.);$ spec. rot. $-53^{\circ} \longrightarrow -42.5^{\circ} (26^{\circ}; c, 5; dry benzene; 10 hrs.).$

Anal. Calcd. for $C_7H_{10}O_6(CH_3CO)_6C1$: Cl. 8.04; saponification value (six equivalents), 13.6 cc. 0.1 N NaOH per 100 mg. Found: Cl, 7.96; saponification value, 13.7 cc.

We are indebted to Mr. John Walker (W. P. A. Project 18062) for assistance rendered in the analytical determinations. We also acknowledge the assistance of Mr. Irving Auerbach (N. Y. A. Project O. S. U. 167).

Summary

1. aldehydo-1-Chloro-1-methoxy-d-galactose

pentaacetate was synthesized by the action of acetyl chloride upon d-galactose dimethyl acetal pentaacetate.

2. aldehydo-1-Chloro-1-ethylmercapto-d-galactose pentaacetate (II) was synthesized by the action of a mixture of acetyl chloride and phosphorus oxychloride upon d-galactose diethyl mercaptal pentaacetate.

3. *d*-Galactose diethyl monothioacetal and *d*-galactose S-ethyl O-methyl monothioacetal and their pentaacetates have been synthesized from II.

Columbus, Ohio

Received January 26, 1940

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

The Thermal Decomposition of Diacetyl

By W. D. WALTERS

In a previous investigation¹ the rate of decomposition of diacetyl in the range 424-470° was obtained by pressure measurements and the products of the reaction analyzed. Since diacetyl can be determined quantitatively by conversion to dimethylglyoxime, which, on addition of a nickel salt, precipitates as nickel dimethylglyoxime, it is possible to analyze for the amount of diacetyl remaining after the decomposition has been allowed to proceed for a definite time. The present work was undertaken to investigate the kinetics of the decomposition by this method, thereby avoiding any assumptions regarding the relation between the pressure increase and the amount of decomposition. The effect of propylene on the rate of decomposition and the variation of the ketene concentration during the decomposition also were studied.

Experimental

The diacetyl, obtained from the Eastman Kodak Company, was dried over calcium sulfate and purified by four fractional distillations under vacuum, the middle twothirds being used for each subsequent operation. The diacetyl used in this investigation was analyzed quantitatively, as indicated later, and found to be pure within the limits of error of the method, $\pm 0.1\%$. The diacetyl was protected from light and between runs kept at -80° . The propylene, obtained from the Ohio Chemical Company, was of 99.5% purity.

The cylindrical Pyrex vessel, 75×120 mm., was contained in a furnace similar in design to the one previously

used.¹ By means of a chromel-alumel thermocouple located at the center of the reaction vessel, the temperature was determined to within 0.1°. A temperature control of $\pm 0.25^{\circ}$ was obtained by causing light reflected from the mirror of a galvanometer in the thermocouplepotentiometer circuit to fall on a photoelectric cell, which controlled additional heating current. All thermocouples were standardized at the boiling point of sulfur and the absolute accuracy of the temperatures measured should be at least $\pm 0.5^{\circ}$. In runs 29-50 inclusive, from which the activation energy was determined, a new thermocouple, standardized before use at the sulfur boiling point and after use against a standard thermocouple, was used every day.²

In order to obtain a pressure of diacetyl in the reaction vessel higher than its vapor pressure at room temperature, a small side arm was connected to the line leading from the storage bulb to the reaction vessel. This Tsection was separated by a stopcock I from the reaction vessel and separated by another stopcock II from the line leading to the storage bulb. To introduce a sample into the reaction bulb, stopcock I was closed and stopcock II opened. Using dry-ice-acetone mixture the desired amount of diacetyl was condensed in the lower part of the side arm. After stopcock II was closed and I opened, the dry-ice-bath was replaced by a heated liquid-bath, vaporizing the diacetyl within fifteen seconds. The external tubing adjacent to the reaction bulb was heated with resistance wire to approximately 85° to prevent condensation of diacetyl. Stopcocks I and II which were also heated were "no-lube" stopcocks ground for high vacuum, and to these it was necessary to apply only a small amount of high vacuum grease. The diacetyl storage bulb was fitted with a small stopcock and ground glass joint so that it could be removed, the grease wiped off the

⁽¹⁾ Rice and Walters, J. Chem. Phys., 7, 1015 (1939).

⁽²⁾ Roeser and Wensel, Bur. Standards J. Research, 14, 277 (1935).

joint with ether, and the bulb weighed without admitting air. These weighings were reproducible to within at least 0.4 mg. To ensure that no trace of air entered the reaction bulb, the diacetyl was outgassed at -80° in the storage bulb and again in the side arm before every run. Moreover, blank determinations showed that under the conditions used no diacetyl was lost. In the runs with propylene the same procedure was followed except that the desired amount of propylene was placed in the furnace prior to the introduction of the diacetyl.

Before using a new reaction vessel, or after contact with air, it was flushed out at an elevated temperature with several charges of diacetyl, one of which was allowed to remain in the vessel overnight. A similar treatment was given the packed bulb, which was filled with thin-walled Pyrex tubes. The reaction bulb was evacuated to a pressure less than 10^{-3} - 10^{-4} mm. before every run.

After a definite time in the reaction vessel, the products of the reaction, as well as diacetyl, were removed by expansion into a condensing apparatus consisting of two long spirals of 8-mm. tubing, a trap fitted with a ground glass joint, and a U-tube in series, all of which could be immersed in a dry-ice-acetone mixture. Since undecomposed diacetyl, which is readily condensable, represented the major portion of the gas in most of the runs, about 85%of the charge could be removed within a few seconds. Then after forty seconds the remainder of the gas in the reaction bulb was led through the condensing apparatus by connecting the U-tube to the pumping system. At -80° all the diacetyl condensed out and the permanent gases and ketene were removed. No diacetyl could be detected in the effluent gases. By noting the pressure in the reaction vessel during removal, a correction could be applied for the decomposition occurring as the charge was being removed. This usually corresponded to about twenty seconds' additional heating. All the diacetyl was distilled into the removable trap, which was then taken off and kept at -80° while a solution of hydroxylamine hydrochloride and nickel chloride was added. Then this bulb was fitted with a ground glass cap and allowed to warm up to 0°. The rest of the analysis for diacetyl was a modification of the method described by Schmalfuss and Rethorn.³ To precipitate quantitatively any nickel dimethylglyoxime remaining in solution after the first filtration, a second period of heating of the filtrate with simultaneous evaporation and subsequent addition of ammonium hydroxide was necessary.

To follow the reaction and determine the time of removal, pressure measurements were made using a heated click gage calibrated before and after every run. The volume of the click gage together with external tubing amounted to about 1% of the total volume. The extrapolated and calculated initial pressures ordinarily agreed to within 1%.

The determination of ketene was accomplished by its reaction with water to form acetic acid, which could be titrated with dilute alkali. The gases from the reaction vessel were removed by expansion into an evacuated 2liter bulb, which was connected to the apparatus by a ground glass joint so that it could be rotated. At the time the gases entered, ice at -80° was contained in a finger attached to the bulb. By quickly melting the ice and rotating the bulb, the water, which ran into the bulb, would cover a large part of the inner surface of the bulb, thus facilitating the reaction between the ketene and the water. In the presence of diacetyl an excess of alkali must be avoided, since in alkaline solutions reactions involving diacetyl apparently destroy a portion of the alkali. However, with continuous stirring the titration of acetic acid in the presence of diacetyl to the brom thymol blue end-point with dilute alkali could be used satisfactorily. Blank determinations using standard acetic acid and diacetyl showed that a small correction of about 1% was necessary.

Results

To determine whether diacetyl undergoes some reaction at low temperatures, a few preliminary experiments with initial pressures in the neighborhood of 150 mm. were made at 114, 242, 304, and 346° with reaction times of sixty-six minutes or more. Within the limits of experimental error no reaction could be detected either from the pressure measurements or from the analyses for diacetyl. The results of experiments at higher temperatures where decomposition does occur are given in Table I. The majority of runs were carried to only small amounts of decomposition, 20% or less, so as to avoid as much as possible any interference by the products. The data from the runs at 408° with initial pressures from 147 to 287 mm. indicate that the fraction decomposed within a certain time is practically independent of the initial pressure. Since similar results over a wider range of initial pressures were obtained in the previous investigation using pressure measurements, first order constants were calculated for all the runs and they are given in the last column of Table I.

In the runs near 418 and 436° which were carried to larger amounts of decomposition, the first order constants decrease as the percentage decomposition increases, indicating that probably the reaction is complex and inhibited to some extent by the products. From the measured pressure increases and the amounts of diacetyl disappearing, it was possible to correlate the pressure increase with the fraction of diacetyl decomposed at 418 and 436°, as shown in Fig. 1. These curves could then be used to transform the pressure measurements during a run into percentages of decomposition. During a single run at either of these temperatures, although the first order

⁽³⁾ Schmalfuss and Rethorn, Z. Untersuch. Lebensm., 70, 233 (1935).

Run	Temp., °C.	Time, sec.	<i>P</i> ₀ , mm.	Δ <i>Ρ</i> / <i>Ρ</i> ₀, %	Diacetyl in bulb, g.	Diacetyl decompn. (anal.), %	$ \times \frac{k_{1 \text{st order}}}{10^5, \text{ sec.}^{-1}} $
			Unpa	icked Bulb			
42	383.1	24205	198.3	20.1	0.2086	17.4	0.788
49	383.1	23850	201.7	19.1	.2121	17.4	.802
39	383.1	23905	210.5	19.6	.2225	16.6	.758
46	391.5	13410	172.9	20.0	. 1786	16.6	1.36
31	391.8	13355	202.7	20.5	.2104	17.6	1.45
35	398.2	8070	204.8	20.6	.2102	16.2	2.19
19	399.1	7280	218.0	19.6	.2236	16.7	2.51
20	399.1	3880	230.1	11.0	.2372	9.4	2.53
36	407.1	4310	213.7	21.2	.2156	15.4	3.87
12	408.0	7750	147.2	34.7	. 1499	29.8	4,56
21	408.0	4330	169.8	23.0	. 1715	17.7	4.50
18	408.0	4670	197.8	24.5	. 2014	19.3	4.59
15	408.0	7630	210.5	34.4	.2141	29.2	4.53
22	408.0	4360	287.0	22.9	.2890	18.3	4.63
47	417.7	10320	218.5	69.0	.2161	53.6	7.44
48	417.7	21650	195.7	100.1	. 1935	74.3	6.27
50	417.7	36505	160.1	119.4	.1572	85.9	5.36
32	418.0	1895	188.1	21.5	. 1866	15.5	8.92
33	418.0	4170	209.6	38.3	.2063	29.0	8.21
38	425.6	1160	196.8	22.3	. 1921	15.7	14.7
37	425.6	1100	226.4	21.1	,2208	14.9	14.6
40	435.8	577	213.6	22.6	.2042	16.0	30.1
41	435.8	628	198.3	23.4	. 1892	16.9	29.5
23	435.9	760	213.4	28.1	.2004	21.1	31.2
24	435.9	1965	209.1	55.3	. 1965	41.8	27.5
25	435.9	3885	237.6	80.2	.2256	60.4	23.9
29	436.2	10855	216.4	124.0	.2043	84.6	17.3
30	436.2	23460	212.2	148.8	. 2028	94.9	12.7
			Pack	ed Bulb ^a			
45	383.1	22635	192.1	20.1	. 1545	19.2	0.943
44	398.2	8055	192.4	20.2	.1508	18.3	2.51
43	425.5	1180	208.5	21.5	. 1571	15.3	14.1

TABLE I DECOMPOSITION OF DIACETYL

" Surface to volume ratio increased eighteen-fold.

constants fall off as the reaction proceeds, the decrease from the initial value does not exceed 5% until more than 25% of the diacetyl has decomposed. However, to fit the experimental results fairly satisfactorily over the whole decomposition, a 1.6 order would be required at 436° and a 1.5 order at 418° .

The results from experiments on the packed bulb with the surface to volume ratio increased by a factor of 18 are also shown in Table I. The rate at 425.5° , although somewhat slower, is essentially in agreement with the rate in the unpacked bulb. At the lower temperatures the rate is slightly faster than the rate in the unpacked bulb, but even at the lowest temperature, 383.1° , where the heterogeneous reaction would be expected to become more important, the rate in the packed bulb is only 20% greater than the rate in the unpacked bulb, indicating about 1% of heterogeneous reaction.

The activation energy was obtained, as shown in Fig. 2, from runs with initial pressures near 200 mm. in which the amount of decomposition was low and approximately constant, averaging about 16%. This procedure will tend to eliminate any errors arising from the falling off of the rate constants as the reaction proceeds, since, as already mentioned, this effect is not appreciable until more than 25% decomposition has occurred. Using the value of 63,200 cal. for the activation energy, the reaction rate constant can be expressed as

$k = 8.7 \times 10^{15} e^{-63200/RT} \text{ sec.}^{-1}$

It is known that ketene is produced during



Fig. 1.—Plot of pressure increase against fraction of diacetyl decomposed: ●, 418°; ○, 436°.

the decomposition of diacetyl,^{1,4} and the reaction which has been proposed for its formation is

 $CH_{2}COCOCH_{3} \longrightarrow CH_{4} + CO + CH_{2} = CO$

Assuming the correctness of this equation, a comparison of the pressure increases in Table I with the amounts of diacetyl decomposed indicates that polymerization of the ketene is occurring. Moreover, the rise of the curves in Fig. 1 near the end of the decomposition points to the presence of an intermediate which decomposes with



(4) Hurd and Tallyn, THIS JOURNAL, 47, 1779 (1925).

an increase in volume. Apparently ketene undergoes decomposition as well as polymerization.⁵ However, it is uncertain whether the polymerization and the decomposition are competing reactions, or, as Hurd and Williams⁶ suggest, the polymerization to acetylketene occurs first, followed by the decomposition of the acetylketene. In any case, it is to be expected that if diacetyl does decompose according to the equation given above, the yield of ketene will increase as the percentage of diacetyl decomposed decreases. The results of the analyses for ketene are shown in Table II and Fig. 3. The percentages of decomposition were obtained from pressure increases using the data shown in Fig. 1 and Table I.

TABLE II						
Ketene	Present	DURING	DIACETVL	DECOMPOSITION		
			This sector 1			

P0, mm.	Time, sec.	$\frac{\Delta P/P_0}{\%}$	Diacetyl decompn. (calcd.), %	$P_{\mathrm{ket.}}/P_{\mathrm{c}},$	Ketene yield, %
		Temp. 4	136°		
214.1	327	12.2	8.6	5.8	67
202.3	609	23.4	16.8	8.7	52
192.4	1965	57.3	43.2	12.0	28
215.5	3850	82.6	62.0	10.0	16
212.5	10840	122.5	83.5	6.5	7.8
211.5	23400	144.3	93.3	4.5	4.8
		Temp. 4	£08°		
204.7	1140	6.1	4.2	2.8	67
195.6	2340	12.2	9.0	4.0	44

Although the highest yield of ketene at 436° was found to be 67% at 8.6% decomposition, the yield of ketene is increasing rapidly and will presumably extrapolate to some value close to 100% at zero decomposition. At the lower tem-



Fig. 3.—Ketene present during the decomposition of diacetyl at 436°: ●, P_{ket}./P₀; ○, % yield of ketene.

(5) Williamson, ibid., 56, 2216 (1934).

(6) Hurd and Williams, ibid., 58, 962 (1936).

perature for the same percentage decomposition a somewhat smaller yield of ketene was obtained. In this connection, it can be seen from the data in Table I and Fig. 1 that as the temperature decreases the pressure increase corresponding to a given amount of decomposition of diacetyl decreases. This fact together with the smaller vield of ketene at the lower temperature may be explained by the increasing importance of the polymerization of ketene as the temperature decreases.

Inhibition by Propylene.--For a number of chain reactions it has been demonstrated that unsaturated compounds, particularly propylene7 and also ethylene,⁸ inhibit the decomposition. In cases where nitric oxide is not satisfactory as an inhibitor, such as the decompositions of aldehydes and ketones, inhibition by propylene has been regarded as an indication of a chain reaction. Therefore, the effect of propylene on the decomposition of diacetyl was investigated and the results of successive runs with and without propylene are shown in Table III.

TABLE III INHIBITION BY PROPYLENE AT 418°

Initial pres P_{Ac_2}	sures, mm. PC3H6	Time, sec.	$\Delta P/P_{\rm Ac_1}$	Diacetyl decompn (anal.), %	$k_{1st order} \times 10^5$, sec. ⁻¹
167.7	100.6	1915	15.0		5.97^{a}
164.1	0	1915	22.0		9.23*
195.9	99.0	1915	15.5	10.7	5.92
191.0	0	1910	21.0	15.0	8.51
193.6	150.1	1920	14.4	10.3	5.66
188.1	0	1895	21.5	15.5	8.92

^a Calculated from pressure increases instead of analyses.

The first two runs, on which only pressure measurements were made, indicated that propylene was definitely an inhibitor. However, to avoid the possibility that the slower pressure increase might be due to some cause other than the slower decomposition of diacetyl, analyses for the amount of diacetyl present, as well as pressure measurements, were carried out in the succeeding runs. For comparison the results of run 32 which had been made earlier are given in the last line of the table. The analytical results, which show that the rate of decomposition is approximately 35% slower in the presence of 150 mm. of propylene, are in agreement with the pressure measurements.

Discussion

On the basis of the inhibition with propylene and also the kinetics of the ordinary decomposition, it would appear that the decomposition of diacetyl is probably a chain reaction. Moreover, the fact that small amounts of diacetyl can promote the chain decomposition of other compounds,⁹ such as diethyl ether, acetaldehyde, and acetone, gives evidence that free radicals are produced when diacetyl decomposes. Although the experimental results do not exclude the possibility that some decomposition occurs through intramolecular rearrangement, it is probable that the major portion of the decomposition is a chain reaction. Therefore, as in the previous investigation, the following simplified chain mechanism for the decomposition of diacetyl, designated by M_1 , will be assumed.

$$M_{1} \longrightarrow 2R_{1} \qquad (1)$$

$$R_{1} + M_{1} \longrightarrow R_{1}H + R_{2} \qquad (2)$$

$$R_{2} \longrightarrow R_{1} + M_{3} \qquad (3)$$

$$R_1 + R_2 \longrightarrow R_1 R_2 \qquad (0)$$

Under conditions where the amount of decomposition according to reaction (1) can be neglected in comparison with the chain decomposition, the rate of decomposition has been shown to be¹⁰

$$\frac{d(M_1)}{dt} = -\sqrt{\frac{k_1 k_2 k_3}{k_4}} (M_1)$$
 (I)

In the presence of an inhibitor, such as propylene, which acts by removal of radicals R₁¹¹ $R_1 + M_3 \longrightarrow X$

the rate equation¹² becomes

$$\frac{\mathrm{d}(M_1)}{\mathrm{d}t} = -\left[\left(\frac{k_1k_2k_3}{k_4} (M_1)^2 + \frac{k_5^2k_3^2}{16k_4^2} (M_3)^2\right)^{1/2} - \frac{k_3k_3}{4k_4} (M_3)\right] \quad (\mathrm{II})$$

That unsaturated compounds are present in the products was shown in the previous investigation, in which the unsaturates were determined as a group including ethylene. From the retarding effect of propylene, these unsaturated products would be expected to exert an inhibiting influence. If the inhibitor, M_3 , in reaction (5) can be identified with one of the products which increases as the amount of decomposition increases, the rate of reaction during a single run would reduce to

 $dx/dt = (k_{\rm A}^2(1-x)^2 + k_{\rm B}^2x^2)^{1/2} - k_{\rm B}x$ (III)

⁽⁷⁾ Rice and Polly, J. Chem. Phys., 6, 273 (1938); 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 and Walters, unpublished results.

⁽¹⁰⁾ Rice and Herzfeld, THIS JOURNAL, 56, 284 (1934).

⁽¹¹⁾ For discussion of possible mechanisms for the removal of

radicals by propylene, see Ref. 7. (12) This equation is similar to equation (36) derived by Rice and Polly.

where x is the fraction decomposed and k_A and $k_{\rm B}$ are constants. At low percentages of decomposition equation III will approach the value given in equation I. Actually the experimental results during a single run at 418 or 436° can be expressed to within 5% by an empirical equation of the above type. This, of course, is a necessary, but not a sufficient, condition to prove the validity of the above equations. The deviation is greatest near the beginning where the rate does not fall off as rapidly as would be predicted from the equation.

Comparison of the fractional times from the pressure measurements for runs at 436° (with initial pressures near 200 mm.) shows that the rates of decomposition in the earlier work¹ are on the average about 9% slower than those obtained in the present study. Most of this difference may be due to a slight difference in temperature scales since a variation of 1° causes a change of approximately 7% in the rate. The present value of 63.2 kcal. for the activation energy is almost within the limits of experimental error of the value 66.5 ± 3 kcal. obtained previously at higher temperatures by pressure measurements, corrected for the change in the pressure increase with temperature. At present it is not possible to state whether the difference is due in part to an increase of activation energy with temperature or is entirely the result of the fact that different methods were used to measure the rate. Although the frequency factor of 8.7×10^{15} is somewhat lower than the earlier value, it is still higher than that found in most decompositions, one outstanding exception being azomethane13 with a frequency factor of 3.5×10^{16} .

Assuming that expression (1) is correct, a high frequency factor might be due to a high frequency factor for one or more of the rate constants in the numerator, or to a small frequency factor for a rate constant in the denominator. On the basis of the Eyring theory¹⁴ of absolute reaction rates, a high frequency factor for a rate constant in the numerator would result if the reaction involved a large entropy of activation.

That there is restricted rotation around the bond joining the two carbonyl groups in diacetyl has been shown by Zahn¹⁵ using dipole measurements, and a similar effect might be expected in a radical with adjacent carbonyl groups. In the

detailed scheme¹ for the decomposition of diacetyl сн.сососн. > POT CO

$CH_{3}COCOCH_{3} \longrightarrow 2CH_{3}CO$	(1)
or	
\longrightarrow CH ₃ + CH ₃ COCO	(1")
$CH_{3}CO \longrightarrow CH_{3} + CO$	(1'a)
$CH_{3}COCO \longrightarrow CH_{3} + 2CO$	(1"a)
$CH_3 + CH_3COCOCH_3 \longrightarrow$	
$CH_4 + CH_2COCOCH$	3 (2')
$CH_2COCOCH_3 \longrightarrow CH_2 = CO + CH_3CO$) (3′)
$CH_3 + CH_2COCOCH_3 \longrightarrow CH_3CH_2COCOCH$	(4')
reactions $(3')$ and $(1')$ assuming for the m	omen

reactions (3') and (1'), assuming for the moment that (1') is the primary reaction, will involve the breaking of the bond joining the carbonyl groups. In both of these reactions a contribution to the entropy of activation would result from the free rotation around this bond in the activated complex. However, with a reasonable estimate of the potential barrier from the dipole data, the entropy of activation, using Pitzer's values,16 although appreciable, does not appear to be sufficient to account entirely for the high experimental frequency factor. By analogy with acetone,¹⁷ any entropy of activation corresponding to free rotation of the methyl groups in the activated complex probably would be small. Moreover, other reasons for a high frequency factor in a chain reaction¹⁸ do not seem applicable to the decomposition of diacetyl.

In trying to decide whether reaction (1') or reaction (1'') is more probable, an attempt was made to estimate the strength of the carbon-carbon bond joining the two acetyl groups using the heats of combustion of diacetyl,19 acetone20 and ethane.²¹ The energy necessary to dissociate diacetyl into two acetyl groups was found to be A + (A - E) - 7 with a possible error of ± 6 kcal., where A is the energy of dissociation of acetone into a methyl and acetyl radical, and E, the energy of dissociation of ethane into two methyl radicals. On account of the variations in the values assigned by different investigators to these carbon-carbon bonds, an attempt to evaluate numerically the above expression at the present time does not seem justified. However, unless there is a large difference in the carboncarbon bond in acetone and ethane, the middle carbon-bond in diacetyl will have a value near that of acetone, in other words, approximately the strength of an ordinary single bond. On the

- (16) Pitzer, J. Chem. Phys., 5, 469 (1937).
- (17) Schumann and Aston, ibid., 6, 485 (1938).
- (18) Rice and Herzfeld, ibid., 7, 673 (1939).
- (19) Landrieu, Compt. rend., 142, 580 (1906).
- (20) Emery and Benedict, Am. J. Physiol., 28, 307 (1911).
- (21) Rossini, Bur. Standards J. Research, 12, 735 (1934).

⁽¹³⁾ Taylor and Jahn, J. Chem. Phys., 7, 470 (1939).

⁽¹⁴⁾ Eyring, *ibid.*, **3**, 107 (1935).
(15) Zahn, *Phys. Rev.*, **40**, 291 (1932).

other hand, LuValle and Schomaker's observations²² of a shortening of 0.07 Å. in the bond between the adjacent carbonyl groups would indicate that this middle bond is somewhat stronger than a single carbon-carbon bond. Although it is difficult to make any decision as to which primary step actually occurs, on the basis of this latter evidence, reaction (1'') would seem to be more probable than reaction (1').

Summary

1. The kinetics of the decomposition of diacetyl between 383 and 436° have been investigated by analyzing for the diacetyl present after

(22) LuValle and Schomaker, THIS JOURNAL, 61, 3520 (1939).

different time intervals. The pressure increases corresponding to the different amounts of decomposition have been determined.

2. With variation of the initial pressure the reaction is first order, but during a run the first order constants fall off.

3. The first order rate constant can be expressed as $k = 8.7 \times 10^{15} e^{-63,200/RT}$ sec.⁻¹.

4. Determinations of the amount of ketene present during the decomposition show that the yield of ketene increases as the percentage of decomposition decreases.

5. Addition of propylene retards the decomposition of diacetyl.

ROCHESTER, NEW YORK RECEIVED DECEMBER 29, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Methyl Chloride¹

By G. H. Messerly and J. G. Aston

This paper presents the results of a low temperature calorimetric investigation of methyl chloride. The work was begun several years ago to permit a comparison between the third law entropy and the value calculated from molecular constants for an organic compound containing methyl groups uncomplicated by the question of restricted rotation. The measurements had to be discontinued, however, because of the destruction by fire of a considerable portion of the Cryogenic Laboratory and have only recently been completed. Egan and Kemp have since published low temperature calorimetric data on methyl bromide and found good agreement between the calorimetric and "spectroscopic" entropy.² Our data on methyl chloride confirm the results of Egan and Kemp with methyl bromide.

Purification of Methyl Chloride.—A commercial sample was used as the starting material. About 150 cc. of liquid was distilled in the absence of air through an efficient vacuum-jacketed low temperature fractionating column (section 1×70 cm. packed with glass helices). An 80-cc. middle portion was redistilled and the middle cut of about 50 cc. after drying over P₂O₅ and removal of the last traces of air, was condensed in a weighed glass sample bulb.

(1) Presented before the Low Temperature Symposium of the Division of Physical and Inorganic Chemistry at the Boston meeting of the American Chemical Society, September, 1939. Vapor pressure measurements taken on the first and last portions of the final sample as the distillation proceeded had shown that no further purification of the material could be effected by fractionation. Two samples from different batches of starting material were prepared in this way. The second of these was used for all measurements. Only the melting point of the first sample was determined.

The Apparatus .-- When the first sample prepared was being cooled to liquid hydrogen temperatures in the apparatus previously described3 most of the apparatus was destroyed by a fire in the laboratory. The rebuilt apparatus was similar to the one destroyed except that the calorimeter itself was made entirely of gold and somewhat larger (present capacity 47 cc.) than the original gold-plated copper calorimeter. Heat conduction was provided for by eight radial vanes instead of the horizontal copper disks previously used. The single standard thermocouple at the bottom of the old calorimeter was replaced by two standard thermocouples which were fastened into horizontal platinum wells gold-welded on the top and bottom of the new calorimeter. The hydrogen liquefier that was an integral part of the old apparatus has been eliminated; liquid hydrogen produced in the laboratory liquefier and other refrigerants are added to the dewar surrounding the cryostat can through a vacuum jacketed german silver transfer tube. The present calorimeter is thus practically identical with the one described by Giauque and Egan.⁴ It will hereafter be designated calorimeter C. The earlier calorimeter, only the winding of which was destroyed, is designated calorimeter

⁽²⁾ Egan and Kemp, THIS JOURNAL, 60, 2097 (1938).

⁽³⁾ Aston and Messerly, ibid., 58, 2354 (1936).

⁽⁴⁾ Giauque and Egan, J. Chem. Phys., 5, 45 (1937).