

CCC.—*The Thermal Dissociation of Carbonyl Chloride.*

By HORACE INGLESON.

THE object of the present work was to obtain satisfactory values for the dissociation constant of a chemical change. As carbonyl chloride dissociates at temperatures sufficiently low to admit of accurate determinations being made, it was decided to study this particular change. Reference to the literature showed serious differences in the results of investigators prior to 1921; these results are summarised in Table I. At the lower temperatures, the values are in bad agreement. Thus, an approximate calculation shows that the value at 341° obtained by extrapolation from Horak's data (Diss., Berlin, 1909) would be of the order of 4000, and not 8280 as calculated from the results of Atkinson, Heycock, and Pope (J., 1920, **117**, 1410). At the higher temperatures, there is a similar lack of agreement among different workers: in nearly every case the results of Atkinson, Heycock, and Pope correspond to a smaller degree of dissociation than that found by other workers.

Bodenstein and Dunant (*Z. physikal. Chem.*, 1908, **61**, 437) used the streaming method in their experiments, and determined the equilibrium both from the thermal combination of carbon monoxide and chlorine and from the dissociation of carbonyl chloride. They

concluded that their results confirmed the theory of Nernst as well as could be expected in the absence of values for the specific heat of carbonyl chloride. Horak (*loc. cit.*) used a quartz spiral manometer in order to measure the pressure developed in a heated porcelain tube filled with the gas, whereas Atkinson, Heycock, and Pope (*loc. cit.*) applied the streaming method to measure the extent of the thermal dissociation of the gas in the presence of a catalyst at temperatures between 101° and 517°.

During the progress of the present work, Christiansen (*Z. physikal. Chem.*, 1922, **103**, 99) published the results of an investigation of the factors affecting the velocity of decomposition of the gas at different temperatures. He concluded that the decomposition was accelerated by the chlorine produced, but his work gives very little information concerning the dissociation constants.

In 1924, Bodenstein and Plaut (*Z. physikal. Chem.*, **110**, 399) described experiments made at temperatures between 373° and 451°, and their results are included in Table I. They were able to confirm the observation of Christiansen that the chlorine accelerates the decomposition.

TABLE I.
Data at present available.

Temp.	K_c .	Author.*	Temp.	K_c .	Author.*	Temp.	K_c .	Author.*
603°	15.0	B.D.	460°	298.7	A.H.P.	404°	1123.0	H.
553	38.0	B.D.	451.3	264.8	B.P.	400	954.6	A.H.P.
506	612.5	A.H.P.	450	343.9	H.	399	1365.0	H.
505	379.0	A.H.P.	449	425.0	A.H.P.	394.6	1230.0	B.P.
505	105.4	A.H.P.	444.1	348.2	I.	389	1409.0	I.
503	78.2	B.D.	443	419.1	A.H.P.	384	2054.0	H.
500	137.5	H.	425	630.7	H.	373.3	1884.0	B.P.
486	209.5	A.H.P.	415	717.9	I.	357	3654.0	I.
481.4	151.6	I.	413.6	719.5	B.P.	341	8281.0	A.H.P.
475	223.9	H.	406	1414.0	A.H.P.			

* B.D. Bodenstein and Dunant. A.H.P. Atkinson, Heycock, and Pope. B.P. Bodenstein and Plaut. I. Ingleson (present paper). H. Horak.

Preliminary Experiments at the Boiling Point of Sulphur.

1. *Chemical Series.*—From a consideration of the difficulties inherent in the streaming method, it seemed likely that some modification of the static method would be more suitable for carrying out the experiments. In the first series of eight experiments, which gave a mean value of $K_c = 354$, a known weight of carbonyl chloride was heated in a closed, thin-walled bulb of glass by suspending it in the vapour of sulphur boiling under atmospheric pressure. At the end of 8 hours, the bulb was quickly removed from the heating bath into a rapid current of carbon dioxide; it was shielded from the light, and the chlorine was determined iodometrically.

This series of experiments and later series in which a similar method was used have been called "chemical." It was decided to control these results by a second set of experiments at the same temperature, based on methods which may be termed "physical."

2. *Physical Series.*—In this series, a glass bulb, filled with a known amount of carbonyl chloride, was heated as before, but the pressure corresponding to equilibrium was measured in a manometer containing mercury after the interposition of an "air buffer." This series gave the value $K_c = 364$ as the mean of eight experiments. Since the agreement of the results of the two series at the boiling point of sulphur was satisfactory, the methods were applied at the boiling point of mercury.

Preliminary Experiments at the Boiling Point of Mercury.

1. *Physical Series.*—The experiments were carried out in the manner just described except that a small amount of charcoal was used to accelerate the rate of attainment of equilibrium. The mean of four concordant results was $K_c = 3007$.

2. *Chemical Series.*—On account of the small extent of decomposition, the chlorine determinations were checked by making careful measurements of the amount of carbon monoxide formed. It was found that the percentage decomposition calculated from the determination of the chlorine was smaller in every instance than that derived from the carbon monoxide measurements; *e.g.*, in one experiment the carbon monoxide measurements indicated 9.1% decomposition (corresponding to $K_c = 3249$), whilst 7.8% decomposition ($K_c = 4429$) was calculated from the chlorine determinations. The means of the values from the chlorine and carbon monoxide determinations were, respectively, $K_c = 4350$ and $K_c = 3181$. It will be seen that the value obtained in the physical experiments, $K_c = 3007$, agrees better with the latter than with the former. As it was clear that the chemical method could not be used with advantage, the physical method was modified so that continuous observation of the pressure of the decomposing gas could be made. By this means, it was found possible to establish the cause of the discrepancy between the two sets of results.

3. *Second Physical Series.*—The apparatus used consisted of a reaction vessel of glass which was joined to a U-tube containing concentrated sulphuric acid. By suitable manipulation of a tap, the U-tube could be made to serve as a manometer which protected the mercury in a second manometer from attack by the chlorine produced in the decomposition. The reaction vessel was filled with carbonyl chloride at room temperature to a convenient pressure, and after the heating of the vapour-bath had commenced, the

levels of the acid in the U-tube were maintained nearly constant by gradually increasing the pressure of the air in one limb of the tube. Readings of the pressure of the gases in the bulb were made at regular intervals after the temperature of the bath became constant. It was expected that the pressure would gradually increase to a constant value, the rate of increase slowly falling to zero. It was found, however, that the rate of increase of pressure did not fall to zero, but only decreased to a small constant value even after prolonged heating had taken place. This suggested that the observed rate of change was not determined simply by the dissociation of carbonyl chloride. On removing the bulb from the heating bath, a marked etching of the inner surface was noticed. The white solid which gave the etched appearance showed the reactions of a chloride.

The results of the eight experiments comprising this series gave an average value of $K_c = 3031$, which is in good accord with the results from the chemical determinations of the carbon monoxide ($K_c = 3181$) and from the first physical series ($K_c = 3007$). These three results lend support to the following explanation of the non-equivalence of the chlorine and carbon monoxide in the chemical series. During the prolonged heating, the materials of the bulb were attacked by the chlorine present and evolution of gas took place. The removal of the chlorine caused a disturbance of the equilibrium and further dissociation of carbonyl chloride took place to re-establish it. Thus, analysis by the chemical method gives a quantity of free chlorine which is too small, whilst the amount of gas determined as carbon monoxide is too large. From this it may be concluded that trustworthy results cannot be obtained in experiments in which the gases are heated for long periods in glass bulbs. A bulb of transparent fused quartz was therefore employed in the later experiments.

Later Experiments.

The results obtained in the five series of experiments made at 357° , 389° , 415° , 444.1° , and 481.4° have been summarised in Table I. Experiments were first made in vapour baths at 357° and 444.1° ; subsequent experiments were precisely similar except that they were carried out in an electric furnace. Those at 389° and 415° were chosen so as to give nearly equal intervals, and when the results at these four temperatures were plotted it was found that a straight line passing through the points corresponding with 357° , 415° , and 444.1° did not pass exactly through that corresponding with 389° . Further experiments were made at 481.4° , which clearly showed that a straight-line relationship exists between

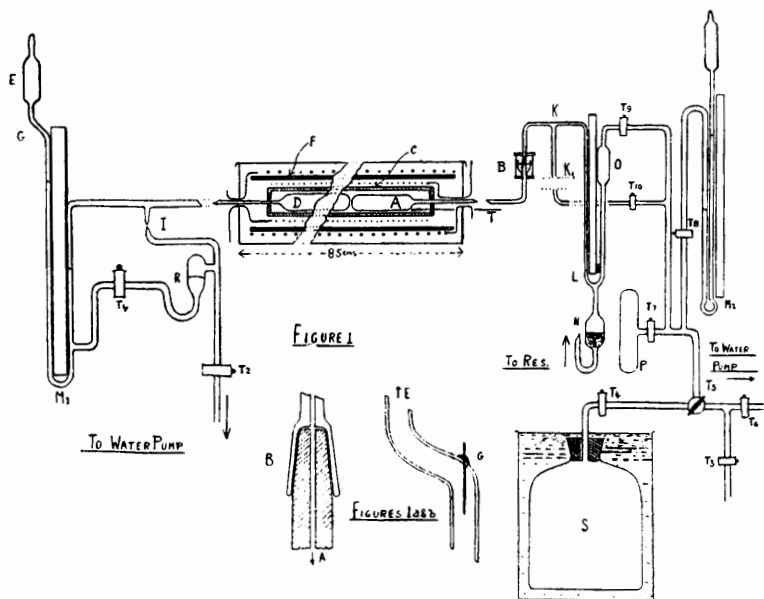
the reciprocals of the temperature and the logarithms of the constants.

EXPERIMENTAL.

The phosgene used throughout was obtained from Kahlbaum in sealed glass bombs. The apparatus is shown in Fig. 1. The quartz bulb, A, had a capacity of about 175 c.c. and was placed inside the heavy copper tube, C. It was joined to the rest of the apparatus through the ground joint, B. This was specially made in order to contain the smallest possible volume (see Fig. 1A), and was lubricated with a thin layer of chlorinated lanoline from which all traces of volatile substances had been removed. The whole was sealed by immersion in mercury, and the two sections of the joint were securely held together. The copper tube was about 65 cm. in length and 5.4 cm. in diameter, and had a wall thickness of 9 mm. Thick copper plates were fixed to the ends of the tube after the bulbs A and D had been placed in position. The tube was evenly wound with heavy gauge nickel-chrome wire, the winding being carried as near to the ends of the tube as possible. The tube F extended beyond the ends of the copper tube for a length of about 8 cm. It reduced the loss of heat from the ends of the copper tube and also kept this tube in an enclosure at a fairly uniform temperature. The tubes were carefully packed in kieselguhr in an iron box. The bulb D was of glass and had a capacity of about 500 c.c. The manometer M_1 carried an evacuated bulb, E, and had a stout platinum wire fused in at G (see Fig. 1B). The T-piece, I, served only in the drying and filling of the bulb, D. The portion of the apparatus just described is called the air-regulator. It served as an air thermometer and also controlled the current supplied to the furnace. The windings round the iron and copper tubes were in parallel and the circuits were so arranged that when that round the copper tube was broken by the operation of the air-regulator, about 2% of the total current was cut off. Fluctuations in the total current caused by changes in the voltage at the laboratory mains were compensated for by the adjustment of a rheostat by hand. This regulation of the current was carried out continuously during the whole time required for an experiment. Observations showed that it was easy to maintain the temperature constant to $\pm 0.25^\circ$ when the temperature of the laboratory was kept fairly constant. The pressure of the carbonyl chloride at room temperature is shown in Tables II and III under the heading p_1 . After the pressure of the air in the large bottle, S, had been adjusted to be nearly equal to p_1 , the tap, T_4 , was closed. The bottle was kept in a well-regulated thermostat. The quartz bulb and all the connecting tubes were repeatedly evacuated and washed

out with the gas before being filled. Air-free, concentrated sulphuric acid was allowed to close the seal, L, and enter O to a convenient height. The pressure of the gas in the quartz bulb was measured on the vacuum-type manometer, M_2 . The heights of the mercury in the manometers were read to 0.1 mm. with the aid of a cathetometer. The temperature of the gas was read on a mercury thermometer, T, graduated to 0.1° , which had been checked at the melting point of ice and at the transition point of the system $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O} - \text{H}_2\text{O}$. After the pressure and temperature of the air in the bulb D had been measured, a nitrogen-filled

FIG. 1.



thermometer was put in position, the tap T_4 was opened and the heating current passed through the furnace. Well-dried air was admitted into S to keep the levels of the acid in the seal nearly stationary and thus compensate for the gradual increase in pressure of the gases in the quartz bulb. During the heating, approximate measurements were made of the pressures of the gases in the bulbs. It was observed that up to about 350° the pressures increased roughly in proportion to their initial values. Then the gases in the quartz bulb began to exert a proportionately greater pressure than did the air in the bulb D. This effect became more and more marked, and the rate of decomposition as deduced from pressure measurements passed through a maximum value after the highest temperature

had been reached. This behaviour is in accord with the observations of Christiansen (*loc. cit.*). When the pressure of the decomposing gas ceased to increase, the experiment was discontinued. Heating of the bulb was in all cases continued for 12—24 hours after chemical equilibrium appeared to have been reached. The pressures corresponding to equilibrium are given in Tables II and III in columns headed p_2 .

In order to provide a check upon the high temperatures employed, air was frequently substituted for carbonyl chloride in the bulb A. Measurements of the quantity pv/T for the quartz bulb and the tubing connected to it were made. The value of T at the high temperature was deduced from measurements of the pressures in the air-regulator. As an example of the values found at the low and high temperatures, a determination at 389° is given: pv/T at $19.2^\circ = 157.7$; pv/T at $389^\circ = 157.5$.

In determining the true value of the concentrations of the gases composing the equilibrium mixture, several corrections were introduced. A small amount of carbonyl chloride in the tubing between the furnace and the meniscus of the acid in the seal was exposed either to bright daylight or to an electric lamp, and thus was not at the temperature of the furnace when the final pressure measurements were made. It is evident that if the equilibrium mixture of gases in the hot bulb could be separated from the gas in the cold tubing and then allowed to regain its original composition and temperature of filling, it would not exert a pressure p_1 , but a smaller pressure.

The separate series of experiments which gave the mean values shown in Table I are discussed below.

TABLE II.

Results obtained at the boiling point of mercury.

No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_e (corr.).	B. p. ($^\circ$ K.)
19	304.57	16.8°	737.66	12.32	3470	629.2°
20	292.78	14.7	712.8	12.92	3778	629.5
21	305.46	15.2	741.3	11.47	3813	630.1
22	301.44	15.3	732.46	11.89	3766	630.9
23	291.25	14.3	714.0	12.24	3633	630.5
24	299.59	20.6	717.9	12.22	3608	629.6
25	304.77	20.6	730.25	12.30	3512	630.25

Mean 3654

Table II gives the results of experiments made at the boiling point of mercury; the alteration of the boiling point with the change in the atmospheric pressure was taken into account. (Data for this correction, and also for that of the series at the b. p. of sulphur, are taken from the *Chemiker Kalender*, 1922, Vol. 2, pp.

129, 130.) The temperature at which each experiment was made is shown in the last column of the table.

It is considered that the results are more trustworthy than any hitherto obtained at 357°. The values of the constant are calculated directly from the percentage decomposition (% Dec.) after the use of the corrections referred to above.

TABLE III.

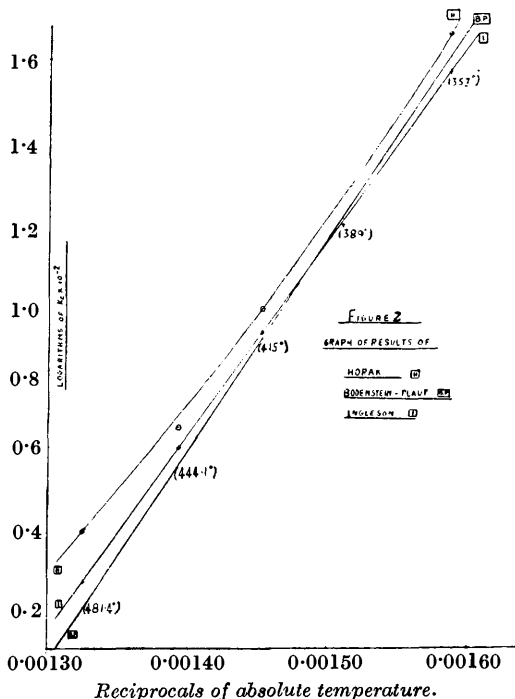
No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_c (corr.).
(a) Results obtained at 388—389°.					
1	271·27	14·9°	748·36	20·55	1248
2	259·5	11·6	722·80	20·36	1319
3	276·34	21·4	747·77	20·46	1118
4	268·89	20·4	729·30	20·63	1273
5	248·23	21·7	667·27	20·34	1432
7	259·87	21·1	703·10	20·56	1352
8	250·76	19·3	680·22	20·22	1423
9	246·06	23·05	662·32	20·79	1373
(b) Results obtained at 415°.					
1	244·80	14·5°	743·10	27·27	720·0
2	231·15	12·6	708·38	27·84	722·1
3	232·20	12·7	710·62	27·71	726·3
4	232·30	12·5	712·90	27·99	707·1
5	231·61	10·5	714·65	27·86	714·0
					Mean 717·9
(c) Results at the b. p. of sulphur (average temp., 444·1°).					
1	206·80	23·6°	692·15	39·14	357·9
2	196·43	18·4	672·03	40·21	345·2
3	203·43	19·3	691·22	39·57	349·6
4	204·22	21·0	687·14	39·48	353·1
5	203·50	16·8	697·08	39·71	343·7
6	204·28	16·0	706·71	41·38	307·5
7	204·20	16·9	698·01	39·26	353·0
8	210·56	15·7	721·04	39·56	335·1
					Mean 348·2
(d) Results at 480·3°, 481·2°, and 482·5°, respectively.					
1	203·25	21·1°	788·41	52·31	158·2
2	184·78	20·2	729·75	54·40	153·5
3	187·00	17·35	751·93	55·22	143·2
					Mean 151·6

Of the experiments in Table IIIa, Nos. 1—4 were made at 388° and the others at 389°. The mean from Expts. 5—9 is $K_c = 1395$, or, excluding No. 7, $K_c = 1409$. It was found that a trace of sulphuric acid had entered the quartz bulb in Expts. 1—4; the effect of this would be to give too large a final reading of the pressure p_2 and thus too small a value for K_c . Furthermore, since the value $K_c = 1409$, from Expts. 5, 8, and 9, approximates more closely to the smoothed curve representing the results at other temperatures (see p. 2252), this value is regarded as the more trustworthy and is quoted in Table I.

A comparison of the results given in Table IIIc (which all relate to temperatures between 443.7° and 444.8°) with the values obtained in the preliminary experiments at the boiling point of sulphur shows a very satisfactory agreement between the three sets of values.

In the graph shown in Fig. 2 the values of $\log K_c/100$ have been plotted against the reciprocals of the corresponding absolute temperatures, the Centigrade temperatures being shown along the

FIG. 2.



course of the graph. The values now found are seen to be approximately intermediate between the most satisfactory values hitherto published. When plotted on a scale sufficiently large to take account of 0.0025 in the logarithms and of 5×10^{-7} in the reciprocals of the temperatures, the points corresponding to the temperatures 481.4° , 444.1° , 415.0° , and 357.0° lie exactly on a straight line. The value of K_c at 389° interpolated from this line is 1429 , whereas the experimentally determined value is 1409 , *i.e.*, about 1% smaller. There is little doubt that the curves of Horak and of Bodenstein and Plaut point to a value of the constant at 357° which is too

large. It is considered that the author's graph reproduces the values of the constant over a range of 120° with considerable accuracy.

Heat of Reaction.

Thomsen ("Thermochemische Untersuchungen," Vol. II, p. 359), in repeating the work of Berthelot on the heat of the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$, measured both (1) the heat change which occurs when carbonyl chloride is passed into aqueous potassium hydroxide, and (2) the heat evolved by the combustion of a mixture of the gas with hydrogen in an atmosphere of oxygen. Berthelot had used the first method and found a value of 18,000 cal., but Thomsen showed that the true value was much higher and obtained results of 26,620 and 25,650 cal. by the two methods. There is thus a difference of 970 cal. between the values given by Thomsen, the mean being 26,100 cal.

The results now obtained have been used to calculate this heat of reaction (Q_v), which has been assumed to remain constant within each temperature-range shown in Table IV. The range (4a) has been included to show the effect upon Q_v and Q_p of using the interpolated value (1429) of K_c at 662° K. instead of the experimental result (1409), which gives the results in range (4). Since Thomsen's data apply at constant pressure at room temperature, the comparison of his results must be made with those shown in col. 3 which are the heats of reaction at constant pressure at the mean temperatures shown in col. 4. The mean of these is 25,500 cal. at an average temperature of 416° , thus differing from Thomsen's mean by 600 cal.

TABLE IV.

Temp. ranges ($^\circ\text{K}$).	Q_v .	Q_p .	Mean temp., $^\circ\text{K}$.
(1) 754.4—717.1	24,030	25,500	735.7
(2) 717.1—688	24,530	25,930	702.6
(3) 688—630	24,340	25,660	659
(4) 688—662	23,620	24,970	675
(4a) 688—662	24,100	25,450	675

It appears doubtful whether this difference between the two values has any real significance as it is within the limits of experimental error in Thomsen's results.

Summary.

The values found by different authors for the dissociation constant of carbonyl chloride show wide divergences, and experiments have therefore been made over a range of 120° —from 360° to 480° . It has been shown that trustworthy results cannot be obtained in experiments in which carbonyl chloride is heated in glass reaction

vessels for long periods. The results obtained in quartz vessels agree fairly well with those of Bodenstein and Plaut.

The values of the logarithms of the constants when plotted against the reciprocals of the absolute temperatures lie on a straight line.

Values calculated for the heat of the reaction show that this changes by an amount less than the uncertainty in Thomsen's values when measured at room temperature and at temperatures between 300° and 500°.

These facts lead to the conclusion that the difference between the sum of the molar heats of carbon monoxide and chlorine and that of carbonyl chloride is constant up to 500°, and that its numerical value is small.

Qualitative evidence was obtained in support of the observations of Christiansen that the decomposition of carbonyl chloride is catalysed by the products of decomposition.

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THE SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE, OXFORD.

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