

Summary

The thermal decomposition of ammonia on pure osmium has been investigated. The reaction was found to be of zero order with respect to ammonia between the temperatures 561 and 640° A. The retarding effect of products is such that the free surface may be represented by a term, $1 - (\text{concentration of products})$ so that the rate equation becomes

$$dx/dt = k(1 - bx)$$

The energy of activation for the given temperature range calculated from half-lives was found to be 47,600 calories per gram mole and calculated from quarter-lives 42,200 calories.

The physical interpretation of these results is that all gases, both products and reactants, are strongly adsorbed, the latter somewhat more strongly than the former.

Adsorption relations on an effective catalyst have been discussed and compared with those found on the effective ammonia catalyst, osmium.

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[CONTRIBUTION NO. 79 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

PHOTOCHEMICAL DECOMPOSITION OF CHLOROFORM

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The correlation of the absorption spectrum of a substance with its photochemical behavior has been the subject of a number of recent investigations. The present work was undertaken to explain the absorption spectrum exhibited by chloroform, which is of a type which has so far been but little investigated.

A number of absorption spectrograms of chloroform vapor have been taken, using a small Gaertner spectrograph, and a hydrogen discharge tube as a light source. They confirm the work of Massol and Faucon¹ in showing absorption only in the far ultraviolet if the chloroform is sufficiently pure. Under the experimental conditions, using only moderate lengths (50 cm.) of chloroform vapor, the red bands found by Russell and Lepraik² and by Ellis³ would not be expected to appear. The absorption found is apparently perfectly continuous, and extends to the limit of transmission of quartz. The long wave length edge is not sharp, and moves toward longer wave lengths with increasing pressure. At the lowest pressures, less than 1 mm. of mercury, the absorption is recognizable at 2300 Å. and becomes total just below 2100 Å. Even with 1 cm. of liquid chloroform, the edge is not sharp, although much sharper, and falls about 2530 Å.

¹ Massol and Faucon, *Compt. rend.*, 159, 314 (1914); *Bull. soc. chim.*, 19, 350 (1916).

² Russell and Lepraik, *J. Chem. Soc.*, 39, 168 (1881).

³ Ellis, *Phys. Rev.*, 32, 906 (1928).

Iredale⁴ has investigated several alkyl halides, and finds a similar continuous absorption. Herzberg and Scheibe⁵ have examined methyl chloride, bromide and iodide very completely, and report a similar continuum, as well as a series of bands still further in the ultraviolet. It is quite possible that similar far ultraviolet bands will be found for many substances, but up to the present so few substances have been investigated in the Schumann region that little is known about them.

The appearance of the continuous absorption is evidence for the dissociation of the molecule. Iredale⁶ has shown that this is the case with ethyl iodide, while Bates and Spence⁷ have recently confirmed the theoretical evidence offered by Herzberg and Scheibe for the dissociation of methyl iodide. Both these substances give free halogen among the products, so that chloroform affords some interesting differences, not all of which can be explained.

If a quartz bulb containing pure chloroform vapor is exposed to a source of far ultraviolet light, such as a brass arc, neither by measurement of the pressure nor by analysis of the exposed gas for chlorine and hydrogen chloride can any evidence of decomposition be found. But if the vapor is streamed past a source of light, and then over an absorbent, decomposition products are found. The explanation seems to be that organic reaction products are deposited on the window in the static system which absorb the light strongly and prevent the reaction from proceeding to a measurable extent. In the moving vapor the deposit should occur downstream from the window, and reaction be recognizable. As evidence for this explanation, it was found in the measurements that the light transmission of the cell for active wave lengths decreased slowly with exposure, even in the dynamic system. It was necessary to remove and clean it about every six experiments, after which the transparency was substantially as before. This change in transparency was taken into account in the calculations.

The decomposition occurring in a stream of vapor does not give rise to chlorine formation. Hydrogen chloride is the only inorganic product, in agreement with the work of Löb⁸ on the decomposition at a hot wire. The quantitative measurements have thus been simplified, and the attempt has been made to elucidate the mechanism of the reaction by a determination of the yield of hydrogen chloride per absorbed light quantum.

Experimental Procedure

Purification of Chloroform.—C. p. chloroform was washed with distilled water to remove the alcohol present (six extractions), dried over calcium chloride, and distilled

⁴ Iredale, *Nature*, **126**, 604 (1930).

⁵ Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

⁶ Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

⁷ Bates and Spence, *THIS JOURNAL*, **53**, 381 (1931).

⁸ Löb, *Z. Elektrochem.*, **7**, 907 (1901).

in a stream of hydrogen. It was then frozen at -78.5° , evacuated and twice fractionated in vacuum, at low temperatures. The final product was stored in a blackened bulb behind a mercury filled U-tube of barometric height. The desired amount of vapor was admitted to the apparatus by lowering the mercury in the U-tube so that the chloroform was not allowed to come in contact with the stopcock grease present on the few stopcocks which convenient manipulation demanded, except during the actual filling of the vessel. The chloroform remained extremely pure during the course of the experiments, as shown by the consistency of the results obtained with several preparations, and by the absorption spectrum. Less carefully purified chloroform was apt to show spurious absorption bands in the near ultraviolet.

Apparatus and Method.—The brass arc mentioned was used only in the qualitative experiments, since it required constant attention, and was extremely irregular in intensity. Attempts were made to use a hydrogen discharge tube, but were abandoned because of the weakness of the source. Finally a condensed spark was arranged, to use either aluminum or zinc electrodes, placed 1 cm. from the reaction vessel. A blast of air between the spark and the vessel served to protect the latter from the heat evolved, and to keep the metal oxide from collecting on the window.

The reaction chamber was made from a cylindrical vessel of fused quartz with flat ends, divided into two drum-shaped sections, 2 cm. in cross section and 8 mm. in depth by a third window parallel to the ends. The light beam passed down the axis of the cylinder, and the chloroform vapor was streamed through the forward chamber. The rear chamber was filled with the photometer liquid. Since the vessel was constructed in the laboratory, the windows were not perfectly plane, though they were reworked after construction to as nearly plane a surface as possible. In particular, the window between the two chambers was made very thin to minimize light losses.

To define the light beam, a diaphragm with an 8-mm. opening was constructed with black paint on the front window of the vessel. The difficulties in obtaining high intensity in this region of the spectrum made the use of the lens and diaphragm system required to obtain a truly parallel beam of light impractical. It is believed, however, that essentially all of the light was received in the photometer cell. Minor variations in the position of the light source did not affect the results, so it is believed that very little light escaped.

Potassium nitrate solution was used as a photometer. It absorbs over much the same spectral region as chloroform, and is decomposed by this light to potassium nitrite with a quantum yield, according to Warburg,⁹ varying from 0.17 at 2530 Å. to 0.25 at 2070 Å. Villars¹⁰ has recently investigated the reaction, and finds higher yields than Warburg, but has not gone to as short wave lengths. Consequently, Warburg's figure of 0.25 has been used in calculating the present experiments, with the knowledge that it is probably low. If this is subsequently found to be the case, the results here presented will have to be raised proportionately.

The potassium nitrate was used as recommended by Gillam and Morton¹¹ as a 0.33 *N* solution buffered with a borate buffer at *pH* 9.4, and the decomposition determined iodimetrically by Villars' method, using 0.001 *N* sodium thiosulfate, restandardized daily. It was found best to keep a stream of carbon dioxide bubbling through the solution during the actual titration, since with such very weak thiosulfate, the end-point was readily affected by air.

Since both chloroform and potassium nitrate absorb over a short range of the spec-

⁹ Warburg, *Sitzb. preuss. Akad. Wiss.*, 1228 (1918); *Z. Elektrochem.*, **25**, 223 (1918).

¹⁰ Villars, *THIS JOURNAL*, **49**, 326 (1927).

¹¹ Gillam and Morton, *J. Chem. Soc.*, **46**, 415T (1927).

trum only, no filters were used. Few lines in the active region were emitted by the light sources, and filters if available would cut down the intensity objectionably.

The light intensity from the spark varied as much as 100% from one run to another, so that a second reference cell was set opposite to that in the circulatory system, and filled with the potassium nitrate solution. Thus the ratio of the decompositions in the two cells with no chloroform present (averaged over blank runs before and after each experiment) permitted the calculation, from the reaction in the reference cell during an experiment, of the light entering the chloroform, while the photometer cell behind the chloroform recorded directly the light leaving the reaction chamber.

In making a run, chloroform was allowed to enter the carefully evacuated system until the desired pressure was reached, and the apparatus sealed off from the reservoir at a constriction, with the chloroform frozen by carbon dioxide snow. The chloroform was re-evaporated, and streamed through the reaction chamber, then over solid potassium carbonate suspended on glass beads, followed by calcium oxide to remove the carbon dioxide formed in the reaction of the potassium carbonate with the hydrogen chloride produced. The purified gas then passed to the circulating pump, and again to the reaction vessel.

At first a pump with a mercury piston was used, but the mercury was gradually attacked, presumably by unsaturated compounds formed in the reaction, so that it was replaced by an all-glass magnetically operated pump. No difference in the results with the two pumps was observed, nor did variations in pumping velocity appear to affect anything other than the speed with which the window of the reaction vessel was rendered non-transparent.

No attempt was made to remove mercury vapor from the system, and since the chloroform was stored behind a column of mercury, it may be presumed to have been saturated with that substance. It does not seem likely that this could have introduced any errors in the experiments, for the light was not of the type to make a photosensitized reaction at all probable, while the possibility of reactions with mercury playing a part in the secondary reactions seems unlikely when the very low concentration of both mercury vapor and of reaction products is considered.

The amount of decomposition was determined at the end of an exposure by washing out the potassium carbonate tube with water, acidifying and precipitating the chloride as silver chloride.

Experimental Results

Table I gives the experimental results obtained for chloroform alone under various pressures, and light sources.

In no case were lower yields obtained. In a number of experiments, particularly the early ones, higher yields were found, but these were always erratic, and could not be duplicated. It is believed that they were due either to faulty analysis in the early cases, or to small accidental traces of oxygen, to which the reaction is extraordinarily sensitive. As will be seen, the yield is independent of pressure over the range used, thus implying complete absorption of the light at all times. Likewise, within the limits of accuracy, it made no difference whether the aluminum spark with its active light of wave lengths 1935 Å., 1989 Å. and 2094 Å. was used, or the zinc spark, which contained the three lines, 2025 Å., 2062 Å. and 2100 Å.

Effect of Temperature.—Only qualitative measurements on the effect of temperature were made. It was difficult from the experimental stand-

TABLE I
 CHLOROFORM RESULTS

Expt. no.	Press. CHCl ₃ , mm.	Time of exposure, min.	Quanta absorbed, einsteins	Moles of HCl, found	Quantum yield	Light sources
9	101.5	31	9.00×10^{-6}	3.42×10^{-5}	3.8	Al
10	95.0	30	5.52	2.09	3.8	
11	97.5	90	11.6	4.18	3.6	
12	100.0	30	6.92	2.65	3.8	
15	50.0	60	6.44	1.74	2.7	
16	46.0	60	5.64	2.30	4.1	
17	53.0	60	6.40	3.00	4.7	Zn
18	49.0	60	4.42	2.02	4.8	
24	52.0	60	2.42	0.84	3.5	
28	99.5	62	3.35	1.40	4.2	
29	49.0	65	4.79	2.30	4.8	
32	52.5	64	1.64	0.63	3.8	
33	101.5	60	2.34	.84	3.7	
42	204.5	60	2.41	.98	4.1	
					Average	3.99

point to devise thermostatic control, and not interpose windows diminishing the light intensity. Consequently, the experiments were made in the open air, and the observation made that the heating of the vapor to approximately 35° from the heating effect of the solenoid which worked the glass pump did not give a yield measurably different from that obtained with the mercury pump where no heat was developed.

Effect of Foreign Gases.—Table II shows the effect of adding, respectively, hydrogen, nitrogen or oxygen (in one case air) to 100 mm. of chloroform.

The earlier experiments showed an increased yield in the presence of hydrogen, though not as great as with nitrogen. But as greater pains were taken to remove oxygen, the yield with hydrogen dropped to a value indistinguishable from that in its absence. The purification of nitrogen is more difficult, and while it is believed that streaming it over hot freshly reduced copper removed substantially all the oxygen, it might be more nearly correct to say that nitrogen probably increases the yield, while hydrogen definitely is without effect on it. An effect of this kind with nitrogen is known in other chain reactions.

Oxygen, on the other hand, accelerates the reaction enormously, even when present to a very small extent. The last column shows that the accelerating effect of oxygen is roughly proportional to the square of the oxygen pressure. In the presence of air, the yield is less than with an equivalent amount of oxygen, showing that the nitrogen is capable of breaking the chains set up by the oxygen, as well as prolonging the chains set up in pure chloroform. This double effect, while not inconceivable, is certainly rather puzzling, and no explanation is offered.

TABLE II
 CHCl₃ + H₂

Expt.	Press. CHCl ₃ , mm.	Press. H ₂ , mm.	Time of exposure, mm.	Quanta absorbed, einsteins	Moles HCl, found	Quantum yield	Light source
37	101.0	104.5	60	1.86×10^{-6}	1.67×10^{-5}	9.0	Zn
40	99.0	100.5	60	1.92	1.67	8.7	Zn
41	100.5	51.0	60	2.97	2.23	7.5	Zn
45	100.5	101.5	60	4.40	1.39	3.2	Zn
49	98.0	55.0	60	3.63	0.91	2.5	Zn

CHCl₃ + N₂

		Press. N ₂ , mm.					
43	99.5	101.5	60	1.78×10^{-6}	3.83×10^{-5}	21.5	Zn
44	100.0	54.5	60	1.16	3.00	25.8	Zn
47	103.5	100.0	60	1.70	4.52	26.5	Zn
48	100.0	54.0	65	1.58	2.92	18.5	Zn

CHCl₃ + O₂

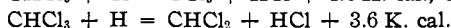
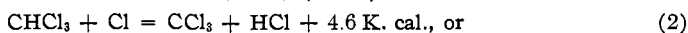
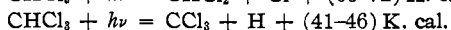
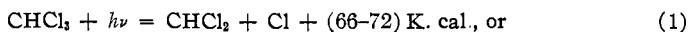
		Press. O ₂ , mm.					Quantum yield/(P _{O₂}) ²
27	99.5	6.5	60	1.77×10^{-6}	1.08×10^{-4}	61	Al 1.5
35	100.0	2.0	60	4.64	4.12×10^{-5}	9	Zn 2.3
38	101.0	18.0	60	0.45	4.13×10^{-4}	922	Zn 2.8
		Air					
26	101.0	101.0	62	2.28×10^{-6}	6.60×10^{-4}	289	Al

Organic Products.—An attempt was made to study the other products of the reaction by rinsing the reaction vessel with pure chloroform, in which the deposit was soluble, and combining the rinsings from a number of experiments. The total quantity thus obtained was still extremely small, and required treatment by micro-chemical methods, for assistance in which the author is indebted to Dr. Erich Mosettig of the Drug Addiction Laboratory of this University. The product from the chloroform solution was subjected to fractional sublimation, and two fractions were obtained. The one crystallized from petroleum ether, and melted at 120–121° with slight decomposition. The other was an oil, which solidified slowly after some days, and on which no melting point could be taken. The properties of these substances do not agree with those of hexachloroethane, tetrachloroethylene or hexachlorobenzene, the three substances isolated by Löb in the work previously cited on the decomposition at a hot wire, and which might be expected to appear here as well. The quantities were so small that it was not possible to proceed further in the identification.

Mechanism of the Decomposition.—A mechanism has been devised for the reaction in the belief that the significant points are best brought out by such a discussion. Unfortunately, the data at hand do not permit of a final decision as to mechanism. The process proposed must, however, involve a primary dissociation of the chloroform molecule by the light absorbed. In the work on alkyl halides cited above, this primary dissociation

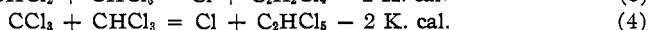
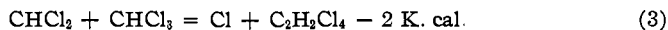
tion has been supposed to be one into a free alkyl radical and a halogen atom. The process may be similar in this case but, due to the large excess energy of the light used, the splitting out of a hydrogen atom is also possible. The fact that no chlorine is found in the exposed vapors does not, as will appear, make its primary production any less likely. One would not expect to find it at the end. Consequently it is assumed that either a hydrogen or a chlorine atom is the primary product of the dissociation.

But whichever is originally produced, it should react on collision with the next chloroform molecule to give a free radical and a hydrogen chloride molecule



(The values of the linkage energies used are taken from the tabulation of Cronheim and Günther¹² in their discussion of the x-ray decomposition of chloroform.)

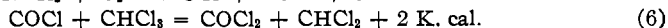
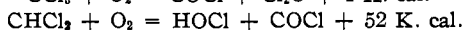
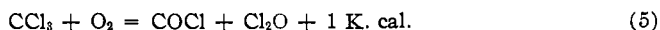
The two radicals thus formed are capable of reaction only when activated, since the reactions are slightly endothermic



However, the necessary energy should be present in the radicals, for the atomic reactions under (2) proceed with an evolution of energy, part of which should be retained by the radical. If this is the case, the atoms produced by reactions (3) and (4) can react as in (2), and a chain process is established which can account for the production of four molecules of hydrogen chloride per quantum absorbed.

This chain will end when the radical loses the necessary energy by a deactivating collision before reaction, the experiments showing that this event occurs after approximately four molecules of hydrogen chloride have been formed. However, such a deactivating process does not explain the effect of nitrogen in lengthening the chains, as opposed to that of hydrogen.

The accelerating effect of oxygen, on the other hand, is easily accounted for. The reaction of a free radical with an oxygen molecule is exothermic



Other reactions with oxygen are possible, but the above meet the qualifications of producing a large yield of chloride, as shown, and also of causing the liberation of iodine from potassium iodide solution, when the gas ex-

¹² Cronheim and Günther, *Z. physik. Chem.*, **B9**, 201 (1930).

posed in the presence of oxygen is streamed into that solution. This effect was obtained in qualitative experiments with the brass arc.

This qualitative agreement does not, however, explain the dependence of the quantum yield in the presence of oxygen upon the square of the oxygen pressure. The experiments show that the effect is unquestionable, but it has not so far been possible to devise an explanation for it.

Some evidence which helps to establish the chain mechanism proposed may be found from a consideration of the photochlorination of chloroform, investigated in the gas phase by Coehn and Cordes,¹³ and in carbon tetrachloride solution by Schwab and Heyde.¹⁴ The former, using light of wave length 4350 Å., find a quantum yield of 1000, while the latter find, even in solution, a yield of from four to fourteen. The writer had attempted to study the gas phase reaction using light of wave length 3650 Å. but after a number of experiments in which no consistency could be obtained between the amount of chlorine used and the amount of hydrogen chloride formed, abandoned the study. The results as obtained, however, were in agreement with the above-mentioned work, for the yield was certainly more than 100.

This reaction is undoubtedly one between chloroform and chlorine atoms, in which the atoms in the chain are most probably regenerated by reaction of the free radicals with a chlorine molecule. This reaction is exothermic, since the linkage energy of the chlorine molecule is only 58.5 K. cal. as opposed to 73 K. cal. of the C-Cl linkage. It then becomes plausible to ascribe the shortness of the chain in the present experiments to the loss of energy necessary for the reactions listed in (3) and (4) since the atomic reactions are shown by the chlorination experiments to be very efficient. Why the necessary energy should be lost when exactly four molecules of hydrogen chloride have been produced is at present not explained.

In that connection it is of interest to recall that Cronheim and Günther¹⁵ in the study of the x-ray decomposition of chloroform also find evidence for a chain reaction long enough to produce approximately four molecules of hydrogen chloride per chain.

Summary

The decomposition of chloroform in the vapor phase when illuminated with far ultraviolet light has been investigated, with the following results.

1. The decomposition proceeds in a streaming system, giving hydrogen chloride, but not chlorine as the inorganic product.
2. The reaction proceeds as a short chain reaction, yielding four molecules of hydrogen chloride per quantum absorbed.

¹³ Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

¹⁴ Schwab and Heyde, *ibid.*, **B8**, 147 (1930).

¹⁵ Cronheim and Günther, Ref. 12; also, *Z. Elektrochem.*, **34**, 616 (1928).

3. The yield is not affected by hydrogen, is probably increased by nitrogen, and very greatly increased by oxygen, in the presence of which, however, the reaction probably proceeds in a different manner.

4. A discussion of the possible mechanism leaves the exact formulation of the reaction unclear, but shows that as far as can at present be established, the results are in accord with other work, and with theoretical considerations.

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

DETERMINATION OF THE FREE ENERGY OF FERROUS HYDROXIDE FROM MEASUREMENTS OF ELECTROMOTIVE FORCE

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The purpose of this investigation was to determine the standard free energy of formation of ferrous hydroxide. This was accomplished by measurements of electromotive force, and the result is compared with others obtained from diverse determinations of the solubility product.

Apparatus and Materials

Measurements were made on a series of cells of the type



in which various samples of iron were used. In addition, a few cells of the type



were included, in which only iron deposited by electrolysis upon platinum electrodes was used. The cells were built with special care to exclude oxygen, and placed in an oil thermostat maintained at 25°. The electromotive forces were measured on the potentiometer described by Lewis, Brighton and Sebastian.¹

Iron.—Four different kinds of iron were used, prepared by the following methods.

(1) Electrolytically, by the Fischer–Langbein process.² The electrolyte was prepared from C. P. hydrochloric acid, pure iron wire in excess, C. P. calcium chloride and distilled water. The iron was deposited upon bright platinum electrodes, 1.3 by 1.3 cm., and pure iron wire served as anode. The electrolysis was performed at the bottom of a U-tube with square corners which was immersed in an oil-bath maintained at 110°, at which temperature practically no hydrogen² is included in the iron depositing on the cathode. In most cases the current density was maintained at 0.15 amp. per sq. cm.

¹ Lewis, Brighton and Sebastian, *THIS JOURNAL*, 39, 2246 (1917).

² Allmand and Ellingham, "Applied Electrochemistry," Longmans, Green and Company, New York, 1924, p. 347.