a small range of temperature. The surface tension data for the above liquids were taken from "International Critical Tables."

DETROIT, MICH. RECEIVED JULY 5, 1934

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

The Photochemical Reaction between Chlorine and Formaldehyde. The Preparation of Formyl Chloride

BY K. B. KRAUSKOPF AND G. K. ROLLEFSON

The thermal reaction between Cl_2 and CH_2O has been studied by Spence and Wild[1] who find that the two gases do not react appreciably at 100°, but form carbon monoxide and hydrogen chloride quantitatively at 150°. The only photochemical process involving gaseous formaldehyde which has been reported is its slow decomposition by ultraviolet light into carbon monoxide and hydrogen, a reaction studied by Bredig and Goldberger[2] and more completely by Norrish and Kirkbride.[3] Spence[4] has found that the polymerization of formaldehyde is unaffected by light of any wave length.

Material and Apparatus

Chlorine was prepared by heating cupric chloride. The gas was stored in a large glass bulb, and was admitted to the reaction vessel by means of stopcocks greased with a mixture of dextrin, glycerin and mannitol. Chlorine so obtained was sufficiently pure to react with carbon monoxide with only a very slight induction period. In a few runs chlorine was evolved from a copper chloride tube sealed directly to the reaction vessel, but no greater purity was obtained by this method.

Of several methods which were used for the preparation of formaldehyde, the one recommended by Spence[4] proved most satisfactory. Dry nitrogen was passed over dried paraformaldehyde (Eastman) or α-polyoxymethylene kept at 120°, and the monomeric vapor was condensed in liquid air and fractionally distilled. To prevent polymerization, it was necessary to keep the formaldehyde frozen in liquid air at all times. Enough of the gas for a run could be obtained by removing the liquid air for a few minutes.

Other gases used in these experiments were obtained by conventional methods. Carbon monoxide was made by dehydrating formic acid with sulfuric acid, and was bubbled through concentrated sodium hydroxide and concentrated sulfuric acid. Hydrogen chloride, prepared by dehydrating a hydrochloric acid solution with sulfuric acid, was frozen in liquid air, fractionally distilled once and stored over anhydrone. Phosgene was distilled from a bomb into a liquid-air trap, fractionally distilled three times and kept as a liquid in a trap surrounded with ice.

The reaction vessel used was a spherical quartz bulb of about 200-cc. capacity, connected to the line by means of a quartz–Pyrex graded seal. For illumination a mercury arc was used in the earlier experiments and a 300-watt tungsten lamp in the later ones.

The strong tendency of formaldehyde to polymerize made it necessary to carry out these experiments at elevated temperatures. Some of the work was done at 60°, but better results were obtained at 80°. To maintain these temperatures, a thermostat with a quartz window was used; tubes leading to the reaction vessel were wrapped with chromel wire and heated electrically. Considerable difficulty was encountered in finding a stopcock grease serviceable at these temperatures and able to withstand the action of chlorine. Apiezon grease was used for a time, but the glycerin–mannitol–dextrin mixture mentioned above proved more satisfactory. It is slowly attacked by chlorine, but apparently no volatile products are formed capable of inhibiting the reaction. The great disadvantage of this grease was the necessity of renewing it after every three or four runs.

The reaction was followed by observing the accompanying pressure change, but the polymerization of formaldehyde made an indirect method of measuring pressures necessary. For this purpose a "click gage" was employed, a thin glass diaphragm on the side of a small bulb, deformed so as to snap into a new position with an audible click when a certain pressure difference is established on its two sides. The gage was connected directly to the reaction vessel, and pressures were read simply by noting the pressure on the outer surface of the gage necessary to make it click. Thus the reaction mixtures were kept entirely within the thermostat, except for one heated side-tube leading to the pumps and gas reservoirs. Click gage readings are reproducible to well under 0.1 mm., but this method of pressure measurement has several disadvantages. The gages, of course, are very fragile; one follows the reaction not directly but by measuring pressures after intervals of illumination; and considerable time is required to make each reading.

Pressures outside the click gage were measured on an α-bromonaphthalene manometer two meters in length. Pressure readings in the following pages will be given in cm. of α-bromonaphthalene; since this substance has a density approximately one-tenth that of mercury, the pressure readings will correspond nearly to mm. of mercury.

Results and Discussion

The primary process in this reaction, whatever source of illumination is used, is the dis-

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[1] Spence and Wild, *Nature*, **132**, 170 (1933).

[2] Bredig and Goldberger, *Z. physik. Chem.*, **110**, 521 (1924).

[3] Norrish and Kirkbride, *J. Chem. Soc.*, **135**, 1518 (1932).

[4] Spence, *ibid.*, 1193 (1933).

sociation of chlorine molecules into atoms. Light absorbed by formaldehyde evidently has little or no effect on the reaction, for runs illuminated with ultraviolet light differ from those illuminated with visible light only in rate.

Ultimately the products of reaction are carbon monoxide and hydrogen chloride. An exact quantitative check on the stoichiometry is impossible because of polymerization of formaldehyde and the gradual formation of phosgene from carbon monoxide and excess chlorine. But a partial proof that carbon monoxide and hydrogen chloride are the chief products can be made by expanding a reaction mixture into a bulb outside the thermostat, freezing the material in this outside bulb with liquid air, and measuring the residual pressure. The amounts of noncondensable gas indicated by such measurements correspond well with the amounts of carbon monoxide assumed to be present.

The only side reactions worthy of consideration are two that have already been mentioned, the formation of phosgene and the polymerization of formaldehyde. The first of these becomes appreciable only toward the end of runs with large excesses of chlorine, and even here its rate is so slow compared with that of the principal reaction that the error introduced probably is not serious. The polymerization of formaldehyde, which occurs to a slight extent at 80°, is a capricious reaction slow enough to be disregarded except in the most sluggish runs. Its rate is usually most rapid immediately after admission of the gas to the reaction vessel, and falls off quickly. The rate is quite unpredictable, although it seems to depend markedly on the formaldehyde pressure.

Another side reaction which must occur to some extent when ultraviolet light is used for illumination is the decomposition of formaldehyde, but under the experimental conditions of this work its rate is negligibly small. A reaction between formaldehyde and hydrogen chloride with the formation of dichloromethyl ether is possible, but apparently it also is slow enough to be safely disregarded. Mixtures of formaldehyde and hydrogen chloride were allowed to stand for long periods, illuminated and in the dark, alone and with small amounts of chlorine present; only very slight pressure decreases were observed which could easily be ascribed to the usual polymerization of formaldehyde.

The formaldehyde–chlorine reaction is very rapid. Comparison of its rate with the rate of the phosgene reaction carried out in the same apparatus indicates a quantum yield of about 10^4 at total pressures of 30–60 cm. Since such long chains are involved, it is hardly surprising that the reaction is extremely susceptible to inhibitors and that accurate reproducibility of runs is almost impossible to attain. The inhibiting action of a few specific gases may be mentioned: carbon monoxide inhibits the reaction slightly, oxygen strongly; phosgene and hydrogen chloride have no effect; mercuric chloride, a powerful inhibitor for the formation of phosgene, produces equally disastrous results in this reaction.

Let us now consider in detail changes of pressure during the reaction. Since three molecules are produced from two according to the equation

$$CH_2O + Cl_2 \longrightarrow CO + 2HCl$$

and since reactants and products are all gases, Δp represents the amount of carbon monoxide formed or the amount of either reactant used up. Plots of Δp against time are not strictly reproducible from run to run, but the general form of the curves does not change. Curve 1 in Fig. 1 is a typical plot for runs with chlorine in excess.

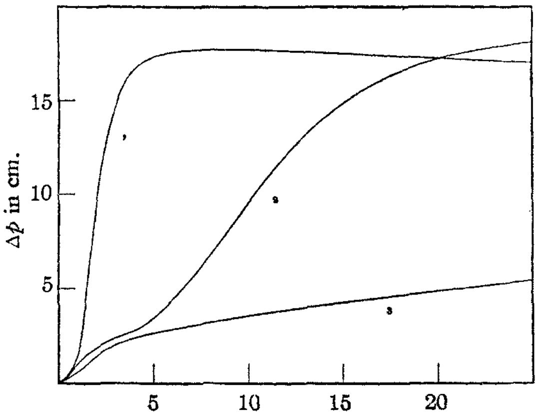

Fig. 1.

The reaction gathers momentum slowly, and reaches a maximum rate when about half the formaldehyde is used up. The gradual decrease in pressure at the end of the reaction is due to phosgene formation.

The slow initial stage of the reaction is variable in length, but never vanishes completely. It is wholly unlike the "induction period" frequently encountered in photochemical reactions, which can be attributed to autocatalysis or to a trace of some potent inhibitor, for the initial portion of this reaction is accompanied by a marked Draper effect. That is, during the first few seconds of illumination the pressure reading is considerably greater when the reaction mixture is illuminated than when the shutter is in place. The Draper effect attains its largest value immediately after illumination is started and then falls rapidly, so that its accurate measurement with a click gage is quite impossible. Its magnitude appears to vary greatly from run to run, but in all cases the effect vanishes completely before the reaction has reached its maximum velocity.

The existence of the Draper effect is conclusive evidence that some reaction is taking place which evolves heat rapidly enough to raise the temperature of the reaction mixture momentarily above that of the thermostat. The reaction producing this effect is obviously not the reaction which forms carbon monoxide and hydrogen chloride, since the Draper effect disappears entirely when this latter reaction reaches its highest rate. Since the Draper effect is largest when the rate curve is nearly flat, it appears that the reaction producing the effect involves no pressure change. Thus the shape of Curve 1 is accounted for satisfactorily by the assumption of two distinct reactions, the first a true photochemical reaction between chlorine and formaldehyde, and the second proceeding only when some necessary intermediate has been produced by the first. The observed pressure change is due entirely to the second, which does not reach its maximum rate until a considerable quantity of the intermediate has been built up.

Unfortunately no convenient method for measuring the rate of the initial reaction has suggested itself. Rough estimates of the rate can be made from the Draper effect; these indicate that the reaction is extremely rapid when the reactants are pure, but that it is highly susceptible to inhibitors. When a mercury pump is used to evacuate the reaction vessel and when special care is taken in purifying the gases, so much heat is evolved by the first reaction that the mixture explodes. The explosion is occasionally so violent that if a moderate excess of formaldehyde is present the excess is decomposed quantitatively into carbon monoxide and hydrogen.

Information concerning the nature of the intermediate formed in the initial reaction may be obtained by a consideration of the changes produced in the rate curve by changing the concentrations of chlorine and formaldehyde. Curve 1, which is the basis for the entire discussion above, is typical only for runs with excess chlorine. When equimolal quantities of the two gases are used or when formaldehyde is present in excess, an entirely different sort of curve is obtained, represented by Curve 3. The Draper effect is observed as before, persisting through the first short, steep rise in the curve; thereafter the reaction proceeds at a rate roughly a hundred times slower than the rates for runs with excess chlorine. Given sufficient time, the reaction with excess formaldehyde eventually uses up all the available chlorine in the formation of carbon monoxide and hydrogen chloride, although there is often a considerable discrepancy in the final pressure reading due presumably to polymerization of formaldehyde. The transition between curves of type 1 and curves of type 3 occurs in a very narrow range of chlorine pressures just above the amount corresponding to an equimolal mixture. For instance, a run made with 20 cm. of formaldehyde and 22 cm. of chlorine gives a plot like Curve 1, while a mixture of 20 cm. of formaldehyde and 20 cm. of chlorine gives one like Curve 3. At intermediate concentrations of chlorine graphs like Curve 2 are obtained.

Only one explanation for the phenomena observed in the transition region seems at all reasonable: by the time the first reaction is complete, the chlorine must be nearly gone. That is, the second reaction in runs like that illustrated by Curve 2 is slow simply because the concentration of chlorine is low and the absorption of light is small. This conclusion is supported by the fact that the addition of chlorine to a run with an initial excess of formaldehyde which has been illuminated for some time causes an abrupt increase in the reaction rate. It follows, then, that the number of molecules of chlorine used up in the first reaction is at least as great as the number of formaldehyde molecules.

A mixture of chlorine and formaldehyde at 80°, as stated before, will not react thermally; but if the mixture is illuminated for even a few seconds, a slow thermal reaction involving a pressure increase sets in. Illumination may be stopped at any point in a run like those represented by Curves 1 and 2, and the slow dark reaction can be observed. Its rate for runs with excess chlorine is practically negligible compared with the photochemical rate. On the other hand, if illumination is stopped after the first few minutes in a run with excess formaldehyde, the reaction continues with rate almost unchanged. That is, the second reaction in runs with excess formaldehyde is practically unaffected by light—another piece of evidence for the assumption that chlorine is entirely consumed in the first reaction in such mixtures. The rate of the dark reaction is dependent on a number of factors, the most immediately evident being the amount of preceding illumination; the rate is largest if illumination is stopped soon after the Draper effect has disappeared. If the light is turned off at or after this point, the dark reaction will proceed to fairly complete formation of carbon monoxide and hydrogen chloride, although if illumination is renewed when the dark reaction is over, a slight further increase in pressure is usually observed. If illumination is stopped before the Draper effect has disappeared, the dark reaction will be proportionately less complete. From these observations we may conclude that the intermediate produced in the first reaction is capable of both a thermal reaction and a chlorine-sensitized photochemical reaction, the products in either case being carbon monoxide and hydrogen chloride.

It is evident by this time that the intermediate under consideration here is a fairly stable substance, able at least to exist for a few hours at concentrations of 3–4 cm. of mercury. Using this fact and the further information that the intermediate must be formed by a process involving no pressure change, we may set down as the only apparent possibilities for the first reaction the three equations

$$CH_2O + Cl_2 \longrightarrow COCl_2 + H_2 \qquad (I)$$
$$CH_2O + 2Cl_2 \longrightarrow COCl_2 + 2HCl \qquad (II)$$
$$CH_2O + Cl_2 \longrightarrow COHCl + HCl \qquad (III)$$

The formation of hydrogen in a photochemical process involving chlorine, as Reaction I indicates, is hardly conceivable. But even if the possibility of its occurrence is admitted, this reaction can be shown not to fit experimental facts. If the phosgene and hydrogen are formed in the initial reaction, the second step must be a reaction between these two, producing carbon monoxide and hydrogen chloride. Now the photochemical reduction of phosgene induced by ultraviolet light has been studied by Montgomery and Rollefson[5] and was found to have a quantum yield between 2 and 3. There is no reason for supposing the yield to be very different when the reaction is started by chlorine atoms from chlorine instead of from phosgene, so it is hard to see how the observed enormous quantum yields of the second reaction could be accounted for. In any event, the hydrogen–phosgene reaction would be far slower than the hydrogen–chlorine reaction if any excess chlorine were present; and if this latter reaction occurred, the stoichiometrical relations would be different from those observed. So Reaction I can be ruled out as a possibility for the first step.

Reaction II is no improvement. In the first place, it requires that twice as much chlorine be used as formaldehyde. Thus when the first step of a run with equimolal quantities of the two gases is complete, the reaction mixture should contain equal amounts of formaldehyde and phosgene. The second step might then be a reaction between these two; but the sharp transition region between Curves 1 and 3 would then be unexplained, for it hardly seems logical to suppose that an equimolal mixture of formaldehyde and phosgene should react much more slowly than a mixture with phosgene in slight excess. A second and conclusive argument against Reaction II is the experimental fact that phosgene will not react with formaldehyde, either thermally or photochemically. Even ultraviolet light has no effect except to dissociate the phosgene.

So by a process of elimination we arrive at Reaction III. The intermediate produced in this reaction, formyl chloride, has not hitherto been isolated. Attempts to prepare it by the methods of organic chemistry result simply in mixtures of carbon monoxide and hydrogen chloride. But its existence has frequently been assumed as an intermediate in organic syntheses, and certainly nothing in the work on this substance would preclude the possibility of its temporary existence as a gas at low concentrations. The kinetic evidence presented above for the appearance of formyl chloride in relatively large amounts in illuminated mixtures of chlorine and formaldehyde seemed good enough to warrant an attempt at its isolation and identification.

For these experiments the static system previously described was replaced by a flow system, in order that the intermediate might be removed from the reaction zone before its decomposition had proceeded too far. Chlorine from a small

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[5] Montgomery and Rollefson, THIS JOURNAL, **55**, 4029 (1933).

storage bulb and formaldehyde from a heated polymer were passed through two flowmeters, allowed to mix, passed through a spiral of glass tubing surrounding a 300-watt tungsten lamp, and finally drawn through a trap immersed in liquid air. In this way formyl chloride, chlorine, formaldehyde and hydrogen chloride were collected in the trap, while carbon monoxide produced by unavoidable partial decomposition of the intermediate was pumped off continually. Chlorine, hydrogen chloride, and a part of the formaldehyde were subsequently removed by pumping on the line with the trap immersed in a carbon dioxide–acetone mixture. The rate of flow of the two gases was adjusted so that chlorine was usually in slight excess, in order to make the amount of formaldehyde in the freeze-out as small as possible; the amount of illumination was regulated to produce the largest possible yield of formyl chloride, this quantity being estimated simply by the amount of effervescence visible when the liquid air was removed from the trap.

Only small amounts of formyl chloride can be produced in this manner, and the substance is always contaminated with liquid and polymerized formaldehyde. Because of the presence of formaldehyde and because of the extreme instability of formyl chloride, a determination of its physical constants was not possible. Evidently it is a liquid at the temperature of carbon dioxide–acetone mixtures (−80°), and even at this temperature it decomposes slowly into carbon monoxide and hydrogen chloride. At slightly higher temperatures the decomposition becomes rapid and the liquid effervesces violently. Apparently decomposition in the liquid phase as in the gas phase is principally heterogeneous, for the vapor is stable enough so that the substance can be distilled from one trap to another, even through considerable lengths of tubing at room temperatures.

Positive identification of the compound was a matter of considerable difficulty. A strong indication of its presence was the fact that the gas produced by the effervescence always observed after a run in the freeze-out trap was only partly condensable in liquid air; the only non-condensable gas which can be formed in this system is carbon monoxide, and there seems to be no way in which carbon monoxide could be retained in the freeze-out trap except in the form of a compound like formyl chloride. A blank run was made using a mixture of formaldehyde, chlorine, hydrogen chloride and carbon monoxide without illumination to see whether carbon monoxide might possibly dissolve in the frozen formaldehyde. Some gas apparently was held in solution, enough to cause slight effervescence when the freezing mixture was removed; but the gas was entirely condensable in liquid air, and therefore contained no carbon monoxide.

Although these observations could hardly be explained without the assumption of formyl chloride, still it seemed desirable to find some reaction which would establish its presence beyond any possibility of doubt. To this end several attempts were made to prepare an aqueous solution of the substance, but rather strangely water in any form appears to catalyze its decomposition instead of hydrolyzing it. The solutions all contained large amounts of hydrochloric acid, but showed only traces of formic acid.

Identification was made possible finally by the preparation of asymmetrical formo-*m*-xylidide, a derivative selected because of its high melting point. A small quantity of xylidine (Kahlbaum) was distilled and placed in a trap so that formyl chloride vapor could be bubbled through it. To the resulting mixture of xylidine, xylidide and xylidine hydrochloride a large amount of ether was added to dissolve the xylidine and xylidide. Dry hydrogen chloride was bubbled through the ether solution until all of the xylidine was converted to hydrochloride, and the solid was filtered off. Evaporation of the filtrate yielded a small amount of xylidide, which was purified by two recrystallizations from water and identified by its melting point. For asymmetrical formo-*m*-xylidide Hodgkinson and Limpach[6] give the m. p. 113.5°. The compound prepared as just described melted at 114–115°; and a sample of the xylidide prepared from formic acid and xylidine showed the m. p. 114°. Identity of the material prepared from formyl chloride with that made from formic acid was confirmed by the fact that a mixture of the two melted at 114.5°.

The preparation of formyl fluoride has been reported recently by Nesmejanow and Kahn.[7] These authors describe the fluoride as a fairly stable substance, boiling at −26° and decomposing slowly at room temperatures into carbon monoxide and hydrogen fluoride. The relatively

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[6] Hodgkinson and Limpach, *J. Chem. Soc.*, **77**, 66 (1900).

[7] Nesmejanow and Kahn, *Ber.*, **67**, 370 (1934).

much greater instability of the chloride is in accordance with the fact that the heavier acyl halides are in general more reactive than the lighter ones.

With formyl chloride as an intermediate, the following picture may be set up for the formaldehyde–chlorine reaction. Illumination starts Reaction III, a highly exothermic process which involves long chains and is accompanied by a large Draper effect in its early stages. The formyl chloride so formed decomposes slowly of its own accord if illumination is cut off, or by a long-chain process initiated by chlorine atoms if illumination is continued. For reaction mixtures with excess chlorine the rate curve starts up slowly and grows steeper as the amount of formyl chloride increases, the maximum slope depending on the amount of chlorine not used up in the first reaction. If enough formaldehyde is present to use up all the chlorine in the first step, the second reaction is merely the slow thermal decomposition of formyl chloride. Whichever reactant is in excess, if the illumination is strong enough and if the gases are pure enough the first reaction may liberate sufficient heat to cause an explosion.

According to this picture the observed "dark reaction" is a spontaneous decomposition of formyl chloride. It appeared quite possible that this decomposition would follow a unimolecular law; in order to check this hypothesis, plots of log $(a - x)$ against time were made for a number of runs. The resulting curves were nearly all straight lines in accordance with a first power law, although a few showed deviations in the direction of a bimolecular law. But the slopes of these lines, and hence the first order "constants," varied enormously from run to run, a fact hardly to be explained on the basis of a simple unimolecular decomposition. At length it was discovered that this decomposition is not a homogeneous process, but depends on the surface of the reaction vessel. Careful cleaning of the vessel increased the first power "constants" by a factor of over twenty, and in subsequent runs the rates declined rapidly toward their former value. Likewise, increasing the surface of the reaction vessel by connecting to it a spiral of Pyrex tubing greatly increased the speed of decomposition. Since the reaction appears to be heterogeneous, the first power curves are illusory and no conclusion can be reached as to the true order of the reaction.

With the data so far obtained for the formaldehyde–chlorine reaction, speculation regarding rate laws and rate mechanisms is rather futile. Pressure readings are subject to unavoidable error not only from formaldehyde polymerization and the phosgene reaction, but from a heterogeneous thermal reaction whose rate at times may amount to a considerable fraction of the photochemical rate. Runs are not reproducible, both because of the variable dark reaction and because of the susceptibility to inhibitors of the long reaction chains. But even if successive runs could be made accurately reproducible, even if errors in pressure readings could be eliminated or allowed for, still the two separate reactions would be difficult to disentangle—especially since the rate of the first cannot be measured easily.

It is not possible even to guess at a rate law for the first reaction, but a little more information is available about the second. By the time a run with excess chlorine has reached its maximum rate nearly all of the formaldehyde present should be converted into formyl chloride, so that from then on the reaction is simply the sensitized decomposition of formyl chloride. Accordingly from the pressure–time curves a rough approximation to the rate law can be derived. Variation of light intensity by means of calibrated screens shows that the rate of this second reaction varies with some power of the light absorbed between 0.5 and 1, probably closer to 0.5. The dependence on the chlorine pressure can be guessed at only by a comparison of different runs, since no chlorine is used up in the second reaction; such a comparison is always unsafe, but a great quantity of data makes it fairly certain that the rate varies approximately with the first power of chlorine. Formyl chloride apparently enters the rate law with an exponent 0.5, so we may write

$$\mathrm{dCO}/\mathrm{d}t = kI^{1/2}_{\mathrm{abs.}}(\mathrm{Cl_2})^{1/2}(\mathrm{COHCl})^{1/2} = k'I_0(\mathrm{Cl_2})(\mathrm{COHCl})^{1/2}$$

Constants obtained from this expression for different runs are illustrated in Table I. The interval selected in each run is the one just after the rate curve has attained its maximum slope. The chlorine pressure in each run is assumed to be the difference between initial chlorine and initial formaldehyde, and the formyl chloride pressure is obtained by subtracting the average Δp over the interval from initial formaldehyde. Admittedly the agreement is not very good, but it is better than for any other rate law which was tried. Agreement of the *k*'s within single runs is illustrated by Table II; the runs selected are the two marked with an asterisk in Table I. The falling off of *k* toward the end of each run is hardly surprising, since every one of the three sources of error in the pressure readings—formaldehyde polymerization, phosgene formation and the thermal reaction—would tend to cause just such an apparent decrease.

Table I

Initial CH_2O, cm.	Initial Cl_2, cm.	Final Cl_2, cm.	COHCl, cm.	Pressure change in 10 sec., cm.	*k*
15.9	19.7	3.8	10.0	1.1	0.92
9.8	14.0	4.2	4.8	1.1	1.20
9.8	14.0	4.2	5.8	1.2	1.19
*16.0	21.6	5.6	9.3	2.4	1.40
10.0	16.0	6.0	6.5	1.4	0.92
14.7	20.9	6.2	8.0	2.3	1.31
16.1	22.4	6.3	11.6	2.6	1.21
15.9	23.1	7.2	7.2	2.5	1.29
14.7	22.1	7.4	8.0	2.0	0.96
*23.6	31.0	7.4	13.2	3.8	1.40
14.6	22.6	8.0	9.9	2.5	0.99
21.2	29.3	8.1	14.7	3.4	1.10
11.7	22.3	10.6	5.6	3.7	1.47
16.1	36.4	20.3	11.2	5.7	0.84

Table II

A			B		
Press. change in 10 sec., cm.	COHCl, cm.	*k*	Press. change in 10 sec., cm.	COHCl, cm.	*k*
2.4	9.3	1.40	3.76	13.2	1.40
2.2	7.0	1.48	3.18	9.7	1.38
1.8	5.0	1.44	2.12	6.8	1.36
1.2	3.5	1.15	1.90	4.5	1.21
0.9	2.4	1.04	1.22	3.0	0.95

The authors would like to express their thanks to Prof. T. D. Stewart and to Dr. D. B. Luten, Jr., for assistance in devising a method for the identification of formyl chloride.

Summary

The photochemical reaction between chlorine and formaldehyde takes place in two steps. The first is an exothermic, long-chain process involving no pressure change. It is accompanied by a marked Draper effect, and under certain conditions may become explosive. One of its products is formyl chloride, COHCl, a semi-stable substance which decomposes in the second step of the reaction into carbon monoxide and hydrogen chloride. The decomposition takes place by a rapid chlorine-sensitized photochemical process if chlorine is in excess, and by a slow heterogeneous thermal reaction if no chlorine is available or if illumination is stopped.

Formyl chloride may be prepared from chlorine and formaldehyde by allowing an illuminated mixture to flow through a liquid air trap. The substance is stable at liquid air temperatures, but decomposes fairly rapidly when brought to room temperature.

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[Contribution from the Frick Chemical Laboratory of Princeton University]

The Weighing of Molybdenum as Silver Molybdate

By LeRoy W. McCay

In a study of the interaction of hydrogen sulfide and molybdic acid, an investigation which has engaged the attention of the writer for a number of years, the need arose for a quick and accurate method for determining the amount of molybdenum in alkali molybdates. For this purpose the precipitation and weighing of molybdenum as silver molybdate has proved to be most convenient.[1] Since the salt is slightly soluble in water a determination of its solubility was made. It was found that 100 cc. of water at 25° dissolve 0.0044 g. of Ag_2MoO_4 (average of four closely agreeing results). It was further found that in water containing a moderate amount of silver nitrate the solubility is practically nil.

The alkali molybdate was dissolved in about 150 cc. of water, a drop of methyl orange solution added and drop by drop enough sulfuric acid to render the liquid just red. A gram of crystallized sodium acetate was then dissolved in the solution, it was heated to boiling, the flame removed and a solution of silver nitrate added slowly with constant stirring until the yellowish-white precipitate, which soon became curdy, had settled sufficiently to leave the solution clear enough to test if more silver nitrate was necessary to complete the precipitation of the molybdenum. While cooling, the solution was stirred thoroughly off and on so that when it had reached room temperature the liquid

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[1] According to Smith and Bradbury silver molybdate and silver tungstate are unsuitable forms in which to weigh molybdenum and tungsten, for both salts are very soluble and decompose on heating (*Ber.*, **24**, 2934 (1891)).