The results given in Table III were obtained by adding air-free stannous chloride solution, at acid concentrations shown in column 2, to excess of the oxidant solution in the presence of air. The excess of oxidant was determined by directly titrating with 0.1 *N* sodium thiosulfate solution, after adding 1 or 2 g. of potassium iodide in the case of potassium iodate. The quantity of stannous tin present, given in column 3, was determined by direct titration with potassium iodate in the absence of air, with proper dilution when necessary.

TABLE III

EFFECT OF ADDING REDUCTANT TO EXCESS OXIDANT

Series	HCl equiv./liter	Stannous present equiv./liter	KIO_3 reduced equiv./liter	KI_3 reduced equiv./liter
A	0.3	0.1043	0.1045	0.1042
B	.6	.09745	.09742	.09748
C	.9	.1466	.1465	.1464
D	1.2	.1008	.1007	.1008
E	3.0	.09776	.09774	.09782
F	4.0	.1061	.1060	.1062
G	6.0	.1076	.1076	.1077

By this order of mixing, both potassium iodate and potassium triiodide give precise results with air-free stannous chloride solutions having hydrochloric acid concentrations even as great as 6 *N*.

Incidentally, some experiments have been carried out to determine the effect of the presence of a few basic constituents, commonly found with tin, on the quantity of iodate required when titrating in the absence of air. Solutions 0.1 *N* in stannous chloride and 1.2 *N* in hydrochloric acid were used. With trivalent antimony present high results were obtained, due presumably to its simultaneous oxidation by iodate. Trivalent arsenic was likewise found detrimental although apparently not as completely oxidized as antimony under these conditions. Copper, added as cupric sulfate, to the extent of 1.2% of the weight of the tin present, produces no error; with 5% copper the error becomes about −0.2%. With 5 % iron, introduced as ferrous ammonium sulfate (free from ferric iron), 0.4% less iodate was required.

Summary

1. Direct titration of air-free stannous solutions with potassium iodate in the absence of air gives precisely the quantity of tin present at acid concentrations as high as 1.5 to 2.0 *N*.

2. With potassium triiodide, appreciable error (about 0.5%) is found even at the lowest hydrochloric acid concentrations used (0.3 *N*). This error may be diminished by decreasing the stannous concentration.

3. When the air-free stannous chloride solution is added to an excess of the oxidant (potassium iodate or potassium triiodide), precise results are obtained at any concentration of hydrochloric acid up to 6.1 *N* without excluding air.

4. The addition of small quantities of nickel or cobalt chloride to the solution reduced by plated-out tin, hastens considerably the redissolving of this tin.

LOS ANGELES, CALIF. RECEIVED DECEMBER 5, 1933

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 389]

The Chlorine-Sensitized Photochemical Oxidation of Chloroform in Carbon Tetrachloride Solution

BY ALAN T. CHAPMAN[1]

The effect of dissolved oxygen on a reaction in which chlorine normally adds to a double bond has been studied in the photo-oxidation of tetrachloroethylene.[2] The simplest example of a compound in which substitution by chlorine may take place is that of chloroform. The photochemical oxidation of this compound was undertaken to ascertain (1) whether or not dissolved oxygen inhibits the chlorination of chloroform,[3] (2) the products of the reaction, and (3) the kinetics of the photo-oxidation. This paper concerns itself with the process in the liquid phase alone. A study of the reaction in the gas phase is now being pursued.

Apparatus

(1) Reaction Vessels.—Figure 1 depicts one of two reaction vessels composed of an illumination vessel A, a 100-cc. bulb B, a well-ground glass joint C, and two sealed-off tips D and E. The flat-walled illumination vessels, each about 1 cm. in thickness, contained 3 and 8 cc., respectively. All portions of the apparatus except the

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[1] National Research Fellow in Chemistry.

[2] Dickinson and Leermakers, THIS JOURNAL, 54, 3852 (1932).

[3] Schwab and Heyde, *Z. physik. Chem.*, B8, 147 (1930).

illumination vessels and the tips were lacquered black. The vessel, supported at joint C, was maintained at constant temperature in a water thermostat.

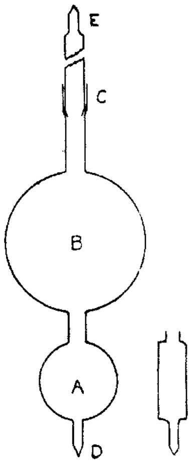

Fig. 1.—Reaction vessel.

(2) **Light Sources.**—For all the preliminary and the majority of the later experiments an ordinary 500-watt incandescent projection lamp was used. Interposed between this light and the thermostat was a water trough containing a filter of 6% copper sulfate solution. The light was placed in series with a variable resistance and an ammeter; the filament was heated gradually and was operated at about 85% of its full current load in order to secure constant intensity over considerable periods of time. The light was collimated by a 16-diopter lens having an aperture of f 1.5.

The photometer described by Leermakers and Dickinson[4] was used to secure monochromatic radiation λ 4358. Corning glasses Noviol A and blue-purple ultra served as additional light filters. The light source in this case was an upright type quartz arc.

Reagents

(1) **Carbon Tetrachloride.**—A good technical grade of carbon tetrachloride was given a preliminary treatment according to the method of Griffin.[5] It was then saturated with chlorine and placed in the sunlight for not less than two weeks. Finally the carbon tetrachloride was subjected to a four-hour treatment with chlorine dioxide, washed with sodium hydroxide solution, barium hydroxide solution, dried over C. P. calcium chloride, and then twice distilled in an all-glass apparatus. A solution of carbon tetrachloride about 0.2 M in chlorine was illuminated in the small reaction vessel, with the projection light. If after eight hours the sample contained more than 1.5×10^{-2} equivalent of acid per liter, it was subjected to further purification.

(2) **Chloroform.**—The chloroform (U. S. P. quality) was purified free from alcohol by one thorough extraction with 9 M sulfuric acid, and six extractions with water. The product was dried over C. P. calcium chloride, and distilled in the all-glass apparatus. Within a week such a sample gave measurable quantities of decomposition products; hence only such portions were distilled as could be used within a few days.

(3) **Chlorine.**—Commercial tank chlorine, purified in the usual manner, was utilized.

Procedure and Method of Analysis.—A 2-cc. sample of the chloroform–carbon tetrachloride solution was pipetted into a flask containing potassium iodide solution; immediately a 3 or 8-cc. sample was introduced into the reaction vessel which was placed in the light thermostat. Frequently the vessel was removed and shaken thoroughly to replenish the oxygen in the solution. The blank solution was analyzed by titrating the iodine with dilute sodium thiosulfate solution. Potassium iodate solution was added; if any acid was detected through further liberation of iodine the sample was discarded.

The solution in the illumination vessel was analyzed with the aid of the apparatus shown in Fig. 2. Flasks F and G contained cold and hot aqueous potassium iodide solution, respectively. The reaction vessel inserted in flask F was completely flushed out by a stream of nitrogen passed into the system through tip D. The complete absorption of phosgene was checked by testing for acid in flask H containing water. The solutions in flasks F and G were analyzed as before except that they were boiled to remove carbon dioxide after titrating the oxidizing strength.

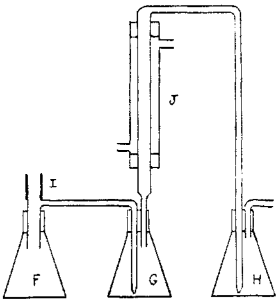

Fig. 2.—Apparatus for analysis.

Inhibition of Chlorination.—Although the analytical procedure was adapted, inherent difficulties in handling chlorine solutions precluded the opportunity of securing precise data to establish completely this inhibition. For critical information two experiments were carried out using the white light for illuminating the sample which was intermittently analyzed by placing in the photometer apparatus. The results of the latter experiment are given in Table I.

TABLE I

INHIBITION OF CHLORINATION BY OXYGEN; OXIDATION COMPLETE IN SIX HOURS

CHCl$_3$ concn., 0.194 M; Cl$_2$ concn., 0.194 M

Time, hours	Transmission	Time, hours	Transmission
0.0	46.3	9.3	46.3
1.0	46.3	15.0	46.3
2.0	46.7	20.0	47.6
3.5	46.7	22.0	47.3
5.0	46.7	24.0	47.3
7.0	46.3		
		Average	46.7

When the agitation of the vessel was omitted, within four hours the transmission had increased to 49.5%. These data offer proof for the fact that within the limits of experimental error the chlorination is completely inhibited.

Products of the Reaction.—When the glass joint of the vessel is opened in the air after four or five hours of illumination the characteristic odor of phosgene is distinguishable. If the sample is treated with titanium sulfate solution the yellow-orange color characteristic of a peroxide appears. No specific tests were applied to determine the presence of hydrogen chloride. No other products of the reaction were detected.

Equivalents of Acid per Mole of Chloroform.—In Fig. 3 the times of exposure in hours

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(4) Leermakers and Dickinson, THIS JOURNAL, 54, 4648 (1932).

(5) Griffin, "Technical Methods of Analysis," McGraw-Hill Book Co., 1921, footnote p. 77.

are plotted as abscissas against the equivalents of acid per mole of chloroform as ordinates. Each one of the curves represents a series of experiments performed as nearly as possible under the same conditions of illumination, chlorine concentration and chloroform concentration; each point on a given curve differs only in the time of exposure. Since these curves are representative of a large amount of data secured over a period of several months, the initial slopes may not be compared with one another. On account of the general linearity of the initial part of each curve, the oxidation rate should be approximately independent of the chloroform concentration.

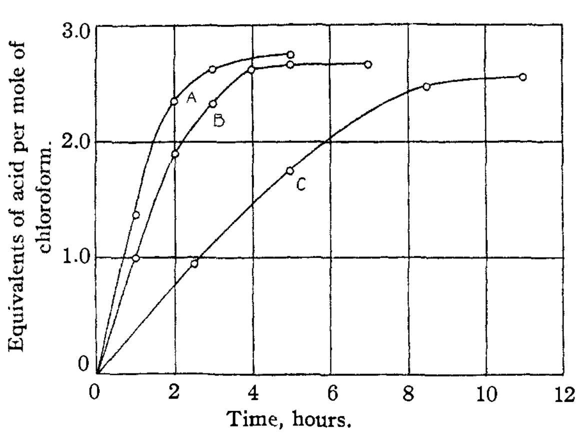


Fig. 3.—Amount of oxidation produced in various times of illumination: A, $CHCl_3$ = 0.020 *M;* Cl_2 = 0.160 *M;* B, $CHCl_3$ = 0.010 *M;* Cl_2 = 0.060 *M;* C, $CHCl_3$ = 0.0685 *M;* Cl_2 = 0.093 *M.*

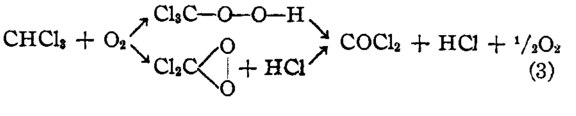
If the oxidation proceeded completely to phosgene and hydrogen chloride according to the reaction

$$CHCl_3 + {}^1/_2O_2 = COCl_2 + HCl \qquad (1)$$

three equivalents of acid (after subsequent hydrolysis) would be obtained per formula weight of chloroform. This yield actually observed varied from 2.5 to 2.8 equivalents of acid per mole of chloroform; hence the oxidation cannot be completely represented by equation (1). However, oxidation to trichloroacetyl chloride

$$2CHCl_3 + {}^1/_2O_2 = Cl_3CCOCl + 2HCl \qquad (2)$$

would give but two equivalents of acid per mole of chloroform. Since positive tests for a peroxide were obtained the course of the reaction may be represented by the equation



$$CHCl_3 + O_2 \begin{matrix} \nearrow Cl_3C{-}O{-}O{-}H \searrow \\ \searrow Cl_2C\langle{}^{O}_{O}| + HCl \nearrow \end{matrix} COCl_2 + HCl + {}^1/_2O_2 \qquad (3)$$

A peroxide such as the latter one, dichlorocarbon peroxide, has been reported in the auto-oxidation of chloroform by Clover.[6] If reaction (3) proceeded only to the peroxide stage, on subsequent analysis with potassium iodide, only one equivalent of acid per mole of chloroform would be obtained. If, on the other hand, reaction (3) proceeded approximately 80% to completion, 20% remaining as peroxide, the observed yield would be accounted for.

The Ratio of Acid to Chloride.—In order to test the validity of equation (2) ratios of total acid to total chloride were determined: this ratio would be 1.33 if trichloroacetyl chloride and hydrogen chloride were the only products. The average acid to chloride ratio as determined from 16 separate experiments was 1.01; of these experiments only one deviated more than 5% from unity. On account of the intrinsic difficulty of subtracting a relatively large number of equivalents of free chlorine from the total chloride as determined from the electrometric titration the 1% above unity is not to be construed as significant.

Investigation of the Peroxide.—Among the available qualitative tests for a peroxide the only one which would give satisfactory results in the presence of chlorine was the reaction with titanium sulfate.[7] Two drops of a 10% solution of titanium sulfate in dilute sulfuric acid was shaken vigorously with 1 cc. of the solution from the illumination vessel and an observation made for the development of an orange-red or yellow color.

The results from eight experiments carried out expressly for this purpose gave five positive tests, two that were questionable and one negative. The exposure time for the negative test was two hours as compared to four or more hours for the others. The more concentrated chloroform solutions gave stronger peroxide reactions. Adequate proof has been obtained that the organic peroxide and free chlorine can exist simultaneously in chloroform solution.

Effect of Moisture.—Every precaution was taken to ensure the thorough desiccation of all reagents. When a trace of water was present a turbidity in the carbon tetrachloride solution was observed which disappeared after a few hours. The moisture was probably consumed in the hydrolysis of a portion of the phosgene.

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[6] Clover, This Journal, 45, 3135 (1923).

[7] See Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1927, Vol. I, pp. 89 and 168.

A short series of experiments was performed in which 0.2 cc. of water was added to the solution at the beginning of the illumination. The results indicate that the reaction proceeded about 1.5 times as rapidly and reached a value of 2.85 equivalents of acid per mole of chloroform in about four hours. The presence of water to some extent accelerated the decomposition of the peroxide, giving a greater yield of acid.

Kinetics of the Reaction.—The effect of various factors on the rate of reaction was determined through a large number of experiments using the projection lamp in the manner previously described. Although experiments with monochromatic light are more desirable, they were dispensed with in view of the fact that exposures would have to be made for a considerably greater length of time.

In all these experiments the small reaction vessel was employed. Calibrated screens were interposed between the light source and the copper sulfate solution in order to vary the light intensity. A comparison of yields with and without Corning yellow filter Noviol A, the aid of an approximate distribution curve for the light source and an absorption curve for chlorine in carbon tetrachloride solution provided the means for a roughly quantitative estimate of the fraction of radiation absorbed. The estimate was placed at 15% for the solutions dilute in chlorine and no greater than 25% for those of stronger chlorine concentration. The general constancy of the yield as given in Table II is indicative of relatively weak light absorption.

From these data the following conclusions may be drawn in regard to the effect of the various factors upon the rate of oxidation.

Oxygen Concentration.—The independence of the rate of oxidation to the oxygen concentration is shown by the coherence of yields in Table II, since no special effort was taken in order to maintain this concentration constant. This result is shown more conclusively by experiments 436 and 437, the former being saturated with oxygen and the latter with air. Other experiments of this type using the large reaction vessel also confirm this conclusion.

Chlorine Concentration.—In certain pairs of experiments such as 369 and 378, 371 and 375, etc., all conditions except the chlorine concentration, which varies about three and one-half-fold, are held constant. The yields throughout are remarkably constant, tending to decrease only in the very highest chlorine concentrations since

TABLE II

EFFECT OF VARIOUS FACTORS ON THE RATE OF OXIDATION OF CHLOROFORM

Expt.	$CHCl_3$, concn. mole/liter	Cl_2, concn. mole/liter, c	Intensity (trans. screen) a	Expt. time, hrs., t	Equiv. acid per cc. $q \times 10^5$	Yield $q \times 10^4/act$
367(25.0°)	0.0484	0.0427	0.677	6.0	1.85	1.06
369		.0519	1.000	2.0	0.958	0.93
371		.0493	0.459	4.0	.971	1.08
372		.0478	.459	2.0	.432	0.98
373		.0487	.459	6.0	1.50	1.11
375		.147	.459	4.0	2.68	0.99
376		.145	.459	6.0	4.13	1.04
378		.147	1.000	2.0	2.66	0.90
379		.146	1.000	4.0	5.82	1.00
380		.147	0.240	2.0	0.723	1.02
381		.139	.240	6.0	1.98	0.99
382		.141	.240	4.0	1.34	.99
383		.140	.103	6.0	0.905	1.05
387	0.247	.0496	1.000	6.0	3.92	1.01
388		.0512	1.000	4.0	1.94	0.95
390		.0526	0.459	5.0	1.27	1.05
392		.0530	.240	4.0	0.490	0.96
395		.0516	1.000	4.0	2.19	1.06
399		.0887	0.459	6.0	2.40–	0.98
401		.107	1.000	6.0	6.73	1.05
403		.109	1.000	2.0	2.22	1.02
407		.105	0.103	4.0	0.460	1.06
410		.109	.103	6.0	.645	0.96
412		.109	.240	6.0	1.57	1.00
413		.162	.240	4.0	1.56	1.00
414		.160	1.000	2.0	2.89	0.93
415		.160	0.459	4.0	2.66	.90
418	.0677	.132	1.000	2.0	2.74	1.04
419		.132	0.459	4.0	2.54	1.05
420	.0917	.127	.459	4.0	2.53	1.08
421		.127	1.000	2.0	2.76	1.09
422	.121	.123	0.459	4.0	2.30	1.02
423		.119	1.000	2.0	2.69	1.13
424	.262	.142	1.000	2.0	3.13	1.10
425		.139	0.459	4.0	3.42	1.34
426	.609	.124	1.000	2.0	2.88	1.16
427		.127	0.459	4.0	2.75	1.18
428	1.222	.156	.459	4.0	2.86	1.00
429		.154	1.000	2.0	3.12	1.01
430	2.498	.200	1.000	2.0	4.43	1.11
431		.199	0.459	4.0	3.72	1.02
432	5.100	.161	1.000	2.0	4.58	1.42
433		.156	0.459	4.0	3.88	1.35
434	12.45	.142	.459	4.0	5.91	2.26
435		.135	1.000	2.0	5.03	1.87
436	0.0247	.0825	1.000	2.0	1.49	0.90
437		.0812	1.000	2.0	1.45	.92
438		.0773	0.459	4.0	1.45	1.02
439		.0763	1.000	2.0	1.63	1.07
440(0.5°)		.0716	0.459	4.0	0.970	0.74
441		.0727	1.000	2.0	1.11	.76
442		.0703	1.000	2.0	2.09	1.49
443 (48.5°)		.0682	0.459	4.0	1.94	1.55

the absorption of light was taken proportional to this concentration. When the absorption is small the rate of oxidation is directly proportional to the chlorine concentration.

Chloroform Concentration.—In experiments 367–437 inclusive the concentration of chloroform has been varied over 100-fold with no evidence for an increased rate of oxidation per unit absorption; even when pure chloroform is employed (a concentration change of over 500-fold) this rate has scarcely doubled. In this case sufficient oxygen does not exist in the solution to inhibit chlorination.

Light Intensity.—The light intensity was varied over a 10-fold range by means of calibrated screens. The aperture was kept constant and the value of the total flux of radiation was arbitrarily taken as the transmission value of the screen. Table II provides ample evidence that the rate of oxidation is proportional to the first power of the intensity of the incident light.

Temperature.—All the experiments in Table II except the last four were carried out at 25.0°. Table III summarizes the information with regard to temperature effects.

TABLE III

TEMPERATURE COEFFICIENT

$CHCl_3$ concn. 0.0247 mole/liter

Temp., °C.	Intensity	Cl_2 concn., mole/liter	Expt. time, hours	Yield $\times 10^4$	$(k_T + 10)/k_T$
0.5	0.459	0.0716	4.0	0.738	1.14
25.0	.459	.0773	4.0	1.022	1.19
48.6	.459	.0682	4.0	1.548	
0.5	1.000	.0727	2.0	0.762	1.15
25.0	1.000	.0763	2.0	1.068	1.15
48.6	1.000	.0703	2.0	1.486	
					Av. 1.16

Quantum Yields.—Since the yields from the oxidation of chloroform employing the white light are not as precise as those from the use of a monochromatic light source, no attempt was made to determine the absolute total flux of radiation. Four experiments were carried out with the photometer previously mentioned. The results are given in Table IV.

The apparatus was set up in a position such that by using the larger reaction vessel all the radiation emerging from an orifice 2.5 cm. in diameter was intercepted by the solution. The thermopile recording the intensity of the direct beam was calibrated. The loss due to reflection was taken into account. In the first two experiments the lamp was not in good alignment with the opening; however, in every case a careful survey of the radiation field was made. No special attempt was made at thermostating since the apparatus was isolated in one room in which the temperature did not fluctuate by more than 0.2°. The system was interrupted occasionally for shaking the solution.

TABLE IV

QUANTUM YIELD DETERMINATIONS AT 21.5°; $\lambda = 4358$ Å.

$CHCl_3$ concn. 0.0247 mole/liter

Intensity ergs/sq. cm. sec.	Time, min.	Fraction absorbed	Total equiv. acid $\times 10^5$	Equiv. acid per einstein
1218	333	0.4825	3.68	1.75
1614	231	.7225	4.83	1.66
645.3	234	.7082	2.09	1.81
707.6	256	.6968	2.15	1.58
				Av. 1.70

The average value of 1.70 equivalents of acid per einstein of radiation absorbed should be accurate to 10%. If about 20% of the reaction proceeds to form a peroxide and 80% to phosgene and hydrogen chloride, 0.65 mole of chloroform is oxidized per einstein of radiation.

Discussion.—The similarity between the chlorine sensitized photo-oxidation of chloroform and the same reaction with tetrachloroethylene is remarkable. The temperature coefficient is practically identical; the reaction rate and the quantum yield are each about 50% smaller; however, both are of the same order of magnitude. Since the reaction rate is governed chiefly by the initial absorption of light by chlorine, it is difficult to explain this difference unless there is some loss of chlorine atoms through recombination either on the wall or on the solvent molecules. The results would then be coherent since the energy required in breaking a C–H bond is appreciably greater than that for the conversion of a carbon double bond to a single bond. Furthermore, the probability of collision of the chlorine atom with the hydrogen of the chloroform molecule (not *a priori* essential) is much less than such a collision with a chlorine atom of the tetrachlorethylene molecule.

No mechanism which explains satisfactorily both of these oxidations has been deduced. Further attempts will be deferred until after the reaction has been studied in the gas phase.

The author takes this opportunity to express his sincere thanks to Professor R. G. Dickinson of this Laboratory for his continued assistance and stimulation given throughout the course of this research.

Summary

Oxygen has been found to inhibit completely the photochemical chlorination of chloroform in carbon tetrachloride solution.

When chlorine is present as a photosensitizer, the oxidation occurs forming principally phosgene and hydrogen chloride; the formation of a peroxide in the course of the reaction is also established.

Employing a white light source under carefully controlled conditions, the rate of oxidation for small light absorption is found to be proportional to the first power of the light intensity, the first power of the chlorine concentration, independent of the oxygen concentration and independent of the chloroform concentration.

The rate of oxidation has been measured at 0.5, 25.0 and 48.6°; the yield increases 16% per ten-degree increase in the temperature.

The average quantum yield for the photooxidation using monochromatic radiation has been determined and found to be 1.70 equivalents of acid per einstein absorbed.

PASADENA, CALIFORNIA RECEIVED DECEMBER 5, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 36]

The Vapor Pressure and Molecular Weight of Chromium Carbonyl

BY MANLY M. WINDSOR AND ARTHUR A. BLANCHARD

All who have proposed or discussed theories of the structure of metal carbonyls[1] have assumed that the molecules of the hexacarbonyls are given by the simplest empirical formulas, $Cr(CO)_6$ and $Mo(CO)_6$. It has been highly desirable to have a definite molecular weight determination to confirm this assumption. According to the theory of Reiff, which is an extension of that originally proposed by Langmuir,[2] if each carbonyl group contributes two electrons to the electron shell of the central atom, chromium, atomic number 24, will possess an "effective atomic number" of 36 if six carbonyl groups are attached to it. Having then the same number of electrons as krypton, the next noble gas, chromium will be like nickel in nickel carbonyl, and the chromium carbonyl should resemble nickel carbonyl rather than cobalt carbonyl (effective atomic number 35) in physical and chemical properties. That is, chromium hexacarbonyl should be monomolecular in the gaseous state, have a relatively high vapor pressure and be sufficiently stable to be capable of sublimation without decomposition. Job and Cassal,[3] who first prepared the compound, found that it could be sublimed *in vacuo*, but a definite knowledge of its vapor pressure over a range of temperature is of sufficient value to warrant its determination in at least the roughly exact manner of this investigation.

The chromium carbonyl used in these experiments was prepared by the action of carbon monoxide upon a suspension of chromic chloride in an ether solution of the Grignard reagent, ethylmagnesium bromide, according to the method of Job and Cassal. The chromium carbonyl was obtained by chilling with solid carbon dioxide and alcohol the ether layer remaining after hydrolysis. It was usually impossible to obtain any product if the ether solution were concentrated by evaporation first, the carbonyl evidently being carried over with the ether vapor. The yields were small, the total amount of pure product obtained from four runs being only about half a gram. The crude material was recrystallized from anhydrous ether, sublimed several times in a sealed evacuated tube and finally sublimed through phosphorus pentoxide into the system in which the measurements were made.

Measurement of Vapor Pressure

Two series of measurements were made, using different modifications of the same type of apparatus. In both cases the compound was placed in a bulb connected to a mercury filled manometer, all of which could be heated in a bath to uniform temperature.

The first apparatus consisted essentially of a manometer made of 8-mm. Pyrex tubing and long enough to support a difference of pressure of one atmosphere. One side was exhausted and sealed. The other side was connected to a small bulb into which the chromium carbonyl was sublimed. With the bulb immersed in a freezing mixture, this side of the manometer was thoroughly evacuated and

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[1] Blanchard and Gilliland, THIS JOURNAL, **48**, 872 (1926); Reiff, *Z. anorg. allgem. Chem.*, **202**, 375 (1931).

[2] Langmuir, *Science*, [N. S.] **54**, 65 (1921).

[3] Job and Cassal, *Bull. soc. chim.*, **41**, 1041 (1927).