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.

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.

(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).

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

sealed. The entire manometer was then attached to a stainless steel meter stick graduated in millimeters and placed in a large vertical jacket. The vapor from a boiling liquid was passed through this jacket until constant temperature was reached. The difference in level of the mercury in the two limbs of the manometer represented the vapor pressure of the substance at that temperature. In this way such factors as the expansion of the mercury and of the metal scale were eliminated except for the actual difference in height. The use of the enclosed manometer obviated the possibility of condensation of chromium carbonyl in a protruding side arm such as would be required with an external manometer.

The temperature was varied by using the saturated vapor of liquids with different boiling points for the heating medium. Starting with ether (b. p. 35°) and substituting other suitable liquids,[4] measurements were made at approximately ten degree intervals up to 135°.
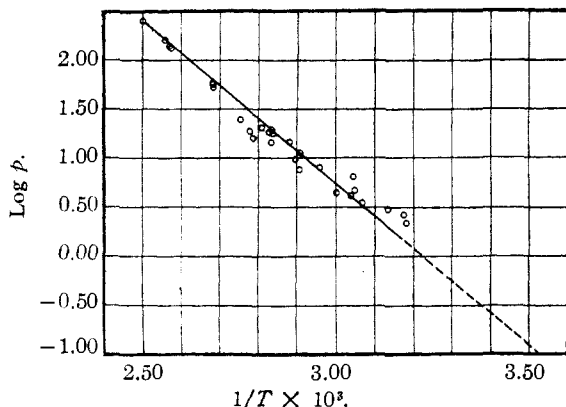

Fig. 1.—The vapor pressure of chromium carbonyl.

In the second series of measurements, a short U-tube filled with mercury was used to seal the tube containing the carbonyl from the manometer, which was placed outside. Both sides of this U-tube were connected with stopcocks to the vacuum line. After subliming the chromium carbonyl into a small bulb, this was attached with an interchangeable ground joint to one side of the U-tube, and the entire apparatus was evacuated using a mercury diffusion pump. The stopcock on the bulb side was then closed and a water-bath placed around the bulb and U-tube. The bath was heated by passing in steam and stirred vigorously to ensure uniform temperature. The vapor pressure of the carbonyl was balanced by admitting air on the other side of the U-tube, and the pressure measurement was read from the outside manometer. Such readings were taken at 10° intervals from room temperature to 97° and also during cooling back to room temperature.

Discussion of Results

The values obtained in a number of determinations using both methods are shown in Fig. 1, where the values of log p are plotted against $1/T$.

(4) The liquids used were, in order of boiling points: ether, carbon disulfide, acetone, benzene and water, pure benzene, n-butyl alcohol and water, water, toluene, n-butyl alcohol, butyl acetate, chlorobenzene and m-xylene.

At the higher temperatures (above 60°) the agreement between different runs is good and the points fall close to the requisite straight line. At the lower temperatures, agreement was poor and the points are all high. This is partly due to the fact that the pressures being measured were small and the errors of reading two or four mercury levels were very large by comparison. Also the possible presence of some residual air or adsorbed gas in the system would make a great difference in the reading obtained. The values obtained by the second method, where more care was taken to prevent residual air, are uniformly lower than those of the first method. As the temperature rose and the pressures increased, this effect of impurities became negligible.

It seems reasonable, therefore, that the actual vapor pressure at the lower temperatures would best be estimated by extrapolating the curve obtained from the higher points. It this is done, the vapor pressure at 20° is 0.26 mm. instead of values around 1 mm. actually found by the second method where errors of reading were large.

The curve in Fig. 1 can be expressed by the empirical equation

$$\log_{10} p = 10.63 - 3285/T$$

The slope of the curve is equal to the constant $\Delta H/R$ in the Clapeyron equation

$$\frac{d \log p}{dt} = \frac{\Delta H}{RT^2}$$

and when solved, the heat of vaporization, $\Delta H =$ 15,180 calories.

A series of values calculated from the curve for a number of even temperatures is given in Table I.

TABLE I

Temp., °C.	0	20	40	50	60	75	80	100
Vapor press., mm.	0.04	0.26	1.35	2.88	5.82	15.28	21.10	66.5

By placing $p = 760$ in the above equation, the temperature at which the vapor pressure would become atmospheric if no decomposition occurred is found to be 151°.

Stability Toward Heat

The first method of vapor pressure measurement used gave a method for detecting the first indications of the decomposition of the chromium carbonyl. In those experiments, the system was cooled back to room temperature between measurements in order to replace one heating liquid with another. If no decomposition had occurred at the temperature attained in the

measurement, the levels in the manometer would return to their former positions at room temperature. On the other hand, if decomposition had occurred, the permanent gas formed would prevent the return to the original pressure.

In this way, evidence of slight decomposition was obtained at as low as 100° in two cases, but the extent was limited. It could be noted with certainty at 116° and was so rapid at 135° that a constant reading of pressure could not be obtained and a mirror of chromium could be observed after a short time.

Determination of Molecular Weight

Evidence as to the molecular formula was obtained in two ways. In two cases, a known weight of the solid was made to vaporize completely at a temperature below that at which noticeable decomposition occurred. The pressure was read and the volume of the entire apparatus subsequently determined. From these data the molecular weight was calculated directly.

In both of these cases, as well as another where the weight of material was not known, after the solid had been completely vaporized and the pressure of chromium carbonyl vapor determined, the heating bath was removed and the tube containing the solid was either warmed gently with a free flame or surrounded with the vapor of boiling methyl salicylate at 230° to decompose the carbonyl completely. The tube was then brought back to the temperature and volume existing before decomposition and the pressure of carbon monoxide determined. The ratio of the pressure of carbon monoxide to that of chromium carbonyl was calculated. From the equation

$$Cr(CO)_6 \longrightarrow Cr + 6CO$$
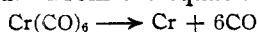
this ratio should be six to one if the compound is mono-molecular, or twelve to one if di-molecular. The results of these measurements are summarized in Table II.

After the experiment, the tube was broken, the deposit of chromium dissolved out, and the amount of chromium determined by the ammonium persulfate method of Hillebrand and Lundell.[5]

(5) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, pp. 410–413.

The volume of the tube was also determined, and the weight of carbon monoxide which would fill it at the temperature and pressure measured was calculated. The ratio of the number of formula weights of CO to that of Cr determines the empirical formula of the carbonyl. These values are also given in Table II.

TABLE II			
Experiment	1	2	3
Temperature, °C.	100	97	97
Volume, cc.	29.6	57.7	65.3
Chromium carbonyl, mg.	..	12.5	5.83[a]
Chromium, mg.	..	2.86	1.35
F. w. Cr	..	0.000055	0.000024
F. w. CO	..	.000317	.00016
Ratio F. w. CO/F. w. Cr	..	5.76	6.60
p Cr(CO)$_6$, mm.	17.3	26	8.5
p CO, mm.	104.2	127	56.3
Ratio p CO/p Cr(CO)$_6$	6.01	4.90	6.60
Mol. weight, found	..	231	242
Mol. weight, calcd.	..	220	

[a] Not determined directly but from the sum of the weights of chromium and of carbon monoxide.

If allowance is made for the small amounts of material used, the results for the ratio of CO to Cr are in good agreement with that required by the formula Cr(CO)$_6$. The molecular weight determinations and also the ratio of the pressures of CO and of Cr(CO)$_6$ show clearly that it is monomolecular. This substance is comparatively volatile, and its stability toward heat is of the order of that of nickel carbonyl and is sufficient for the substance to sublime without decomposition at reduced pressure. These properties link it with the monomolecular Ni(CO)$_4$ rather than with the almost non-volatile and considerably less stable [Co(CO)$_4$]$_2$.

Summary

The molecular formula of chromium carbonyl is Cr(CO)$_6$.

The vapor pressure from room temperature to 125° has been measured and an empirical equation derived.