THE CHEMISTRY OF CHROMYL COMPOUNDS

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Received June 21, 1957

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I. INTRODUCTION

A. EARLY LITERATURE

The substances designated as chromyl compounds in this review have been known for over one hundred thirty years. An extensive literature exists, for their reactivity has been the inspiration for numerous investigations. Yet, in addition to the usual treatment in the standard reference works dealing with chromium, there exists only one brief bibliography (39), one review article by Ridley (202) in 1924 dealing with their properties in general, and two reviews (56, 204) of the Étard reaction,—one by Étard in 1881 and another by Rohde in 1901. The recent announcement (27) of the availability of chromyl chloride as an article of commerce has focused attention on this group of compounds, their physical and chemical properties, and the need for a comprehensive and critical review of the literature.

B. DEFINITIONS AND NOMENCLATURE[2]

For the purpose of this review, the term "chromyl compound" will be limited to compounds of the general formula CrO_2X_2, where X is a univalent acid radical. While the compounds of chromium(VI) oxide and sulfur trioxide (85, 195) are sometimes referred to as chromyl sulfates, these compounds, being solids, are quite different from the subjects of this review. The chromyl compounds as defined above are generally volatile liquids having nonpolar characteristics and

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[2] In accordance with recommended nomenclature, the names listed below are used for the compounds indicated:

CrO_3 = chromium(VI) oxide
CrO_2 = chromium(IV) oxide
$CrCl_2$ = chromium(II) chloride
$CrCl_3$ = chromic chloride or chromium(III) chloride
$CrCl_4$ = chromium(IV) chloride
NO_2 = nitrogen dioxide
N_2O_4 = dinitrogen tetroxide
N_2O_5 = dinitrogen pentoxide

thus can be readily treated as a group. The editors of *Chemical Abstracts* and of *Inorganic Syntheses* prefer the nomenclature "chromyl" for compounds of this type. However, the Stock nomenclature, giving the alternate name "chromium(VI) dioxy," is sometimes encountered. Thus, *Inorganic Syntheses* (224) lists "chromyl chloride [chromium(VI) dioxychloride]." In this review, the chromyl terminology will be used.

C. KNOWN CHROMYL COMPOUNDS

The chromyl group has been reported to form compounds with all the halogens, and with the nitrate, cyanate, and thiocyanate groups. Of these, the chloride CrO_2Cl_2 is the best known, having been first prepared by Berzelius in 1824 (16), although he believed it to be a higher chloride. It was soon shown that the compound contained oxygen (207, 209), and numerous other workers in the early nineteenth century went on to investigate the compound and abundantly confirm its existence as a chemical entity.

Evidence for chromyl fluoride was obtained by Unverdorben (248, 249) at practically the same time as Berzelius' discovery of the chloride; however, he believed it to be a chromium fluoride. The fluoride remained little investigated and it is only recently (50) that its true properties have been determined.

The nitrate has been recently reported (219). Its preparation has been checked in this laboratory and it appears to be a definite chemical compound.

Chromyl bromide has likewise been isolated within the past few years (273, 274). The modern work corrects earlier reports of the compound (77).

While there has been one report of the formation of chromyl iodide as a deep red liquid from a mixture of dichromate, iodide, and sulfuric acid (87), a majority of observers (77, 96, 128, 196, 255) deny this observation and the existence of the compound. There is little likelihood that the iodide can exist, in view of the large free-energy change attendant on the reaction:

$$2Cr^{+6} + I^- \rightarrow I^{+5} + 2Cr^{+3}$$

Solutions of the cyanate in carbon tetrachloride are stable, but decompose with mild explosion on concentration at 55°C. (71). The thiocyanate exists for a short time in carbon tetrachloride solution.

Consideration of the relative oxidizing power of chromium in the hexavalent condition and of the stability of various univalent anions toward oxidation suggests the possibility of the existence of chromyl azide and chromyl perchlorate. The extreme instability of hydrogen azide and anhydrous perchloric acid, which presumably exist as intermediates during the reaction, would undoubtedly make the preparation hazardous and difficult.

D. GENERAL CHARACTERISTICS OF CHROMYL COMPOUNDS

Physically, chromyl compounds are volatile materials, but there are wide differences in both the volatility and the liquid range of the well-characterized chromyl compounds. The most volatile, the fluoride, is a solid at room temperature but sublimes at atmospheric pressure at 29.6°C. The chloride has vapor pressure characteristics resembling those of water but remains liquid to −96.5°C. The nitrate is only slightly volatile, remains liquid to −25°C., and decomposes at about 135°C. without reaching a true boiling point. As liquids, all these compounds are mobile, dark red in color, and miscible with chlorinated solvents. The chloride is a nonconductor of electricity, and presumably the other compounds are also. The chloride and fluoride are stable when properly stored, but the nitrate slowly decomposes.

Chemically, they are all hydrolyzed readily to chromium(VI) oxide and the appropriate acid. In air, the hydrolysis product is a fine aerosol containing either chromic acid mist or solid chromium(VI) oxide, depending on the humidity. The rate of hydrolysis in water depends on the solubility and the temperature; chromyl chloride is hydrolyzed only slowly by cold water, while the more polar and hence more soluble nitrate and fluoride are rapidly hydrolyzed. Other important chemical reactions show the oxidizing properties of these compounds. In the pure state they ignite phosphorus, ammonia, amines, alcohols, and many hydrocarbons. Because of their nonpolar nature, they are inert to most metals. Sodium, as an extreme example, can be immersed in chromyl chloride without any reaction other than the formation of a chromate film.

The most important oxidation reaction is the Étard reaction, in which a chromyl compound, in an inert solvent, combines with an organic compound to form addition compounds which may then be hydrolyzed, usually producing aldehydes or ketones. The reaction may be complicated by secondary reactions such as chlorinations in the case of chromyl chloride. Other oxidations can also be produced. Chromyl compounds are also suitable as starting points for the preparation of chromium(III) coördination compounds. These reactions are discussed in detail in the sections which follow.

II. METHODS OF PREPARATION AND PURIFICATION

A. PREPARATION

Chromyl chloride was prepared by Berzelius (16) by distilling a mixture of a chromate, sodium chloride, and sulfuric acid. For the chromate, many workers used potassium chromate (20, 53, 207, 253, 269), while others employed lead chromate (42) or potassium dichromate (55, 141, 169, 241). When potassium dichromate was used, it was customarily fused with the sodium chloride before treatment with sulfuric acid. Still other variations employed (*1*) stannic chloride, potassium dichromate, and sulfuric acid (71) and (*2*) calcium dichromate, sodium chloride, and fuming sulfuric acid (123). The latter reaction is claimed to be particularly suited for the production of colored smokes for pyrotechnic and military use.

Certain chlorides are reported not to yield chromyl chloride on treatment with sulfuric acid and a chromate. These are the chlorides of the noble metals (platinum, gold, silver, mercury) and antimony(III) oxychloride (153).

Closely allied to the above reactions is the production of chromyl chloride by the action of sulfuric acid on a chlorochromate such as $KCrO_3Cl$ (188) and the use of hydrogen chloride instead of sodium chloride (192).

In all of the above preparations, the chromyl chloride formed is customarily separated from the solid salt residue by distillation. Heating chromyl chloride in the presence of sulfuric acid causes side reactions with production of chromic sulfate and evolution of chlorine, so that yields by any of the procedures described above are customarily less than 50 per cent.

Improved methods for the preparation of chromyl chloride avoid this difficulty by the use of chromium(VI) oxide, hydrochloric acid, and sulfuric acid. It has been reported that a 35 per cent yield of chromyl chloride can be obtained by the action of 35–40 per cent hydrochloric acid on chromium(VI) oxide; lower concentrations of hydrochloric acid led to lower yields, with evolution of chlorine and formation of chromic chloride (5). The experiments of the authors failed to yield chromyl chloride by the action of aqueous hydrochloric acid on chromium(VI) oxide, but yields of 70 per cent or more can be obtained by the action of dry hydrogen chloride on the oxide (43, 120, 166, 167, 168). By adding sulfuric acid to the reaction mixture and keeping the mixture cool, it is possible to separate a layer of chromyl chloride in yields of 90 per cent or better (117, 120, 145, 146, 216, 225). This layer of chromyl chloride can be removed and purified without danger of side reactions due to the presence of sulfuric acid.

A modification of this process is described in the patent literature (126). In an example, 280 parts of chromium(VI) oxide are allowed to react with 122 parts of 99 per cent sulfuric acid and 1720 parts of recycled 90 per cent sulfuric acid in a water-jacketed reactor at 35–55°C.; then 216 parts of anhydrous hydrogen chloride are added below the surface, keeping the temperature below 55°C. The reaction is complete in 45 min., producing a lower layer of 412 parts of chromyl chloride (97.2 per cent yield) and an upper layer of 90 per cent sulfuric acid, of which 1720 parts are recycled.

Chloro acids or acid chlorides, such as chlorosulfonic acid, have been used in the preparation of chromyl chloride. The general use of these compounds has been patented (189, 190, 191), the process further providing for isolating the chromyl chloride in an inert solvent such as carbon tetrachloride. The reaction of chlorosulfonic acid and chromium(VI) oxide to give chromyl chloride has been described (120), but there is a tendency for excess chlorosulfonic acid to decompose chromyl chloride with formation of a solid product containing chromyl sulfates. A patent for the formation of smokes describes the reaction between ammonium dichromate and chlorosulfonic acid (123):

$$(NH_4)_2Cr_2O_7 + 4ClSO_3H \rightarrow 2CrO_2Cl_2 + 2NH_3 + 3H_2SO_4 + SO_3$$

(See, however, the reaction between chromyl chloride and ammonia in Section IV,D,2.) The reaction of chromium(VI) oxide with other acid chlorides to give chromyl chloride has been described: viz. oxalyl chloride (1), phosphorus pentachloride (217), acetyl chloride (77), and pyrosulfuryl chloride (210). The latter reaction is also carried out with chromates.

In analytical chemistry, the use of perchloric acid and hydrochloric acid or a chloride to react with a chromium(VI) compound and volatilize chromyl chloride is well known (15, 228). The reaction has not been generally used for the preparation of the compound because other, more convenient methods exist.

Other reactions have been listed yielding chromyl chloride. In general, they are inconvenient, yields are poor, and in some cases (indicated by ?) it is doubtful whether significant quantities of chromyl chloride would be obtained. These reactions are *(1)* the passage of hydrogen chloride into chromium(VI) oxide in glacial acetic acid (156); *(2)* the heating of chromium(IV) oxide with carbon tetrachloride in a sealed tube (157); *(3)* the action of chlorine on uncalcined Cr_2O_3 (?) (164, 165); *(4)* the action of moist chlorine on chromates (166, 167, 168); *(5)* the action of oxygen on chromium(II) chloride (?) (166); *(6)* the heating of $(CrO_2)_5Cl_6$ (185) [see p. 19 regarding $(CrO_2)_5Cl_6$]; *(7)* the heating of chromium(VI) oxide in chloroform and oxygen vapor (51); *(8)* the heating of chromium(VI) oxide with ferric chloride or aluminum chloride (81, 82, 83).

The preparation of chromyl fluoride has received far less attention. Most workers in this field used the reaction between a fluoride, a chromate, and sulfuric acid to volatilize chromyl fluoride (68, 131, 181, 206, 248). The fluoride used was calcium fluoride, and the chromate was either potassium dichromate or lead chromate.

Other reactions reported to give chromyl fluoride are the action of iodine pentafluoride on chromium(VI) oxide (6), of antimony pentafluoride on chromyl chloride (213, 214), of fluorine on chromyl chloride at 200°C. in an alumina tube (256), and of anhydrous hydrogen fluoride on potassium dichromate (265) and chromates (72, 73, 89, 265). However, none of these reactions have apparently produced chromyl fluoride in either good yield or high purity, and in some cases no compound was isolated.

The work of Engelbrecht and Grosse (50, 95) in characterizing and purifying chromyl fluoride is outstanding. Their process consists in allowing chromium(VI) oxide to react with a large excess of anhydrous hydrogen fluoride at room temperature. On cooling to −78°C., a crude chromyl fluoride crystallizes and the water formed is removed in the liquid HF phase. The crude crystals may be purified by melting and refreezing, when further HF and water can be separated, and by distilling through a tube packed with sodium fluoride or potassium fluoride, when the last traces of hydrogen fluoride are removed as $Na(K)F \cdot HF \cdot CrO_2F_2$. By this means, a pure chromyl fluoride is obtained which is stable on storage, whereas the impure material prepared by earlier procedures was not stable and possessed variable physical and chemical properties. The red vapors obtained by the earlier workers were in most cases not analyzed and were assumed to be CrO_2F_2 by analogy with chromyl chloride, although as late as 1893 Mendelejeff (155) believed the product to be chromium hexafluoride.

In attempting to prepare chromyl bromide by the action of chromates on bromides in the presence of sulfuric acid, Rawson (196) and Rose (208) obtained negative results. However, by the action of anhydrous hydrogen bromide in carbon tetrachloride on chromium(VI) oxide or dilute chromyl chloride in carbon tetrachloride, or of acetyl bromide on chromium(VI) oxide in glacial acetic acid or chromyl chloride in carbon tetrachloride, a deep transient purple color resembling that of permanganate is observed, which has been ascribed to the presence of chromyl bromide (77). This color was later used as an indicator in studying the action of chromyl chloride on phosphorus halides (78); similar colors were formed from the action of boron tribromide, silicon tetrabromide, and stannic bromide on chromyl chloride in carbon tetrachloride (71). This color was ascribed to addition compounds by Zellner, who finally isolated red-brown needles of chromyl bromide, contaminated with 7.5 per cent of chromyl chloride, by the action of a tenfold excess of liquid hydrogen bromide on chromyl chloride at -60°C. to -80°C. Chromyl bromide decomposes at room temperature and could not be further purified (273, 274).

Although Giraud (87) reported chromyl iodide to be formed by the action of sulfuric acid and potassium iodide on a chromate, other workers (71, 77, 128, 129, 196, 208, 255), using various techniques, have obtained no evidence of the existence of the compound. It is therefore presumed not to exist.

Chromyl cyanate (or more probably chromyl isocyanate) has been prepared in carbon tetrachloride solution by the action of silver isocyanate on chromyl chloride. The deep red solution, containing only traces of the original chromyl chloride, could be evaporated under reduced pressure but decomposed with a weak explosion and flash of light as the last of the carbon tetrachloride was removed (71).

$$CrO_2(NCO)_2 \rightarrow CrO_2 + 2CO + N_2$$

Chromyl (iso?)thiocyanate exists for a short time in solution. It is prepared by the action of $PO(SCN)_3$ on chromyl chloride in carbon tetrachloride solution, giving a turbid solution which later turns dark purple. Substitution of silicon thiocyanate for the phosphorus compound leads to evolution of heat and feeble explosion with the formation of chromic compounds. It is believed that the purple color may be due to addition compounds (71).

Chromyl nitrate is obtained as a deep red liquid by the action of dinitrogen pentoxide on chromyl chloride, potassium chlorochromate, or chromium(VI) oxide (219). The preparation from chromium(VI) oxide and dinitrogen pentoxide has been substantiated in this laboratory (43).

Chromyl acetate is prepared in impure form by the reaction of chromyl chloride in carbon tetrachloride and silver acetate. A brown precipitate is formed with disappearance of the red color of chromyl chloride. However, no reagent was found which would separate silver chloride from the desired product. On hydrolysis, chromic and acetic acids were regenerated from the brown, lustrous powder of chromyl acetate (77). Because of the change in color from the red color characteristic of other chromyl compounds, the apparently nonvolatile product formed, and the insolubility in carbon tetrachloride, it is questionable whether this "chromyl acetate" is a true chromyl compound. Its general behavior is more typical of the addition compounds formed in the Étard reaction (see Section IV,E,2,(a)).

B. PURIFICATION

Of the reported chromyl compounds, only chromyl fluoride, chromyl chloride, and chromyl nitrate have been prepared in the pure condition. The purification of chromyl fluoride (50) by recrystallization from hydrogen fluoride and distillation of the vapors through potassium fluoride has been discussed.

The principal impurities in chromyl chloride prepared by the usual methods, for instance, the two-layer separation described in *Inorganic Syntheses* (119), are hydrogen chloride, chlorine, chromium(VI) oxide, sulfate, moisture, and reduced chromium compounds. Chromyl chloride tends to purify itself of water, since the hydrolysis products react to form chlorine and reduced chromium compounds, which absorb water and are insoluble and therefore readily separated. Hydrogen chloride and chlorine are removed by distillation (145, 169); chlorine is removed by aspiration with air (145) or by shaking with mercury (169). Sulfate is present to the extent of perhaps 0.5 per cent in all chromyl chloride prepared using sulfuric acid or its derivatives. It is not readily separated; fractional distillation in a sixty-plate column removes only part of the sulfate (43). Consequently, chromyl chloride of high purity is best prepared from low-sulfate raw materials, for instance, by the action of hydrogen chloride on chromium(VI) oxide, even at some sacrifice in yield. Chromium(VI) oxide remains behind in the still residues and hence is removed by distillation. If reduced chromium compounds are present, they likewise remain in the still (275).

Suitably purified chromyl chloride has been used for determining the atomic weight of chromium (88).

Preliminary investigations show that chromyl nitrate can be purified by distillation under reduced pressure. The distillate from a crude sample at 45°C. and 2 mm. gave an analysis conforming very closely to the theoretical values (144).

III. Physical Properties of Chromyl Compounds

A. DENSITY

Density data are available only for chromyl chloride; they have been obtained by several investigators, most of whom are in reasonable agreement in spite of undoubted variations in the purity of the chromyl chloride used. The equation selected,

$$d = 1.959 - 1.913 \times 10^{-3}t + 1.797 \times 10^{-6}t^2$$

fits all data reasonably well except that at 10°C. (see table 1).

TABLE 1

The density of chromyl chloride

t	d (observed)	d (calculated)	$d_o - d_c$	Reference	t	d (observed)	d (calculated)	$d_o - d_c$	References
°C.					°C.				
−47	2.052	2.053	−0.001	(161)	21	1.910	1.920	−0.010	(241, 242)
0	1.959	1.959	0	(161)	25	1.912	1.912	0	(161)
0	1.961	1.959	+0.002	(232)	25	1.915	1.912	+0.003	(39)
0	1.965	1.959	+0.006	(69)	25	1.920	1.912	+0.008	(232)
10	1.913	1.937	−0.024	(230)	116	1.758	1.761	−0.003	(232)

The above equation also shows greater accuracy for the more recent determinations (43, 169); it gives values with an accuracy compatible with existing data. Other equations which have been suggested contain terms which are not justified by the data (130) or are less accurate (74).

The specific gravity of the vapor has been determined, with the following results:

Temperature, °C.	127	143.7	147	181	200
Specific gravity (air at same temperature = 1.0)	5.35	5.9	5.69	5.31 ± 0.18	5.39
Reference	(38)	(241)	(38)	(161)	(22)

At 181°C. sufficient replicate determinations were obtained to permit calculation of the standard deviation of the determinations. In view of the fact that the determinations at 143.7°C. and 147°C. represent very early work, the specific gravity of chromyl chloride can be judged to be 5.33 over the temperature range studied. This corresponds to a molecular weight of 154.5, from which it is concluded that the vapor is unimolecular (calculated value of formula weight = 154.92). A similar conclusion is obtained from electron diffraction measurements.

B. MELTING POINT

The violet-red crystals of chromyl fluoride melt at 31.6°C. under a vapor pressure of 885 mm. (50).

Measurements of the melting point of chromyl chloride have not been made with high accuracy, since a thermometer calibrated only in whole degrees was used. A figure of −96.5°C. ± 0.5° is reported for this constant (169).

The melting point of chromyl nitrate is uncertain. It was reported by Schmiesser and Lutzow (219) as about −70°C. However, material carefully redistilled under vacuum was found to freeze to red crystals on cooling to −35°C. The crystals melted at −25° to −30°C. (43). If the liquid is cooled rapidly below its melting point, it becomes very viscous at about −50°C. and under these conditions crystallization does not occur spontaneously.

C. BOILING POINT

Liquid chromyl fluoride exists only at pressures in excess of 760 mm. The orange-red liquid has its triple point with vapor and solid, as mentioned above, at 31.6°C. and 885 mm. The solid sublimes at 29.6°C. and 760 mm. to a reddish brown vapor (50). Earlier work, indicating boiling points below 0°C. or around 80°C. (256, 265), was based on impure materials.

A large number of values have been reported for the boiling point of chromyl chloride. These values, corrected to 760 mm. where necessary by means of the vapor pressure curve, are given in table 2.

The value of 116.7°C. (169) has been accepted by reference works (76, 130). However, the illustration of the apparatus used by these workers shows that the thermometer was placed close to the surface of the liquid and that no frac-

TABLE 2

Boiling point of chromyl chloride

Boiling Point	Reference	Boiling Point	Reference	Boiling Point	Reference
°C.		°C.		°C.	
117.4	(21)	116.7	(161)	116.8	(232)
115–116	(69)	118	(166)	115.9	(233)
116–118.5	(137)	118	(171)	118	(241)
108	(157)				

tionating column was employed during the distillation. Under these conditions there is a definite possibility of superheating because of lack of establishment of equilibrium between liquid and vapor. Consequently, a new determination of the boiling point was made in this laboratory, using a precision column of about sixty theoretical plates (43). The value obtained for the boiling point was 115.7°C.

Chromyl nitrate decomposes when heated at atmospheric pressure before the boiling point is reached. At about 135°C. an endothermic reaction occurs and there is an apparent boiling at nearly constant temperature, but the products are principally chromium(VI) oxide and nitrogen oxides with a small amount of chromyl nitrate vapor (43). Chromyl nitrate may be distilled under reduced pressure; at 0.001 mm. the boiling point is reported as 28–30°C. (219). Preliminary investigations indicate that this volatility may be much too low; observations of the authors show a boiling point of about 45°C. at 2 mm. pressure.

D. VAPOR PRESSURE

Vapor pressure determinations have been reported on both solid and liquid chromyl fluoride (50). For the solid, the vapor pressure is given by the equation:

$$\log_{10} p \text{ (mm.)} = 6.25189 + \frac{959}{T} - \frac{599333}{T^2}$$

This equation gives a pressure substantially higher than an earlier report (256) of a pressure of 24 mm. for the solid at 0°C. The vapor pressure of the liquid, over a narrow range (31–38°C.), is:

$$\log_{10} p \text{ (mm.)} = 8.80494 - \frac{1785.5}{T}$$

The vapor pressure of chromyl chloride has been shown to conform to the Lorenz equation (150). However, only a single set of data is available on the vapor pressure curve of chromyl chloride (169), from which various workers have compiled smoothed data (130, 236). These data are consistent, giving an excellent plot of log p against $1/T$. However, the correction of the atmospheric boiling point referred to in the previous section dictates an adjustment of the data to give the following corrected boiling-point equation:

$$\log_{10} p \text{ (mm.)} = 7.723 - \frac{1883}{T}$$

These data were obtained between 79.4°C. and 120.4°C. Extrapolated values for the vapor pressure have been calculated down to −18°C. (236).

The vapor pressure–temperature relationship calculated by the original experimenters (169) presents temperature as a quadratic function of pressure. It leads to absurd results outside the range of data given and should be discarded.

E. HEAT EFFECTS ACCOMPANYING CHANGE IN STATE

From the equations given in Section III, D the following heat effects have been calculated (50) for the changes in state of chromyl fluoride.

$$CrO_2F_2(s) \rightarrow CrO_2F_2(g), \quad \Delta H = 13{,}800 \text{ cal./mole at } 31.6°\text{C.}$$

$$CrO_2F_2(l) \rightarrow CrO_2F_2(g), \quad \Delta H = 8{,}200 \text{ cal./mole at } 31.6°\text{C.}$$

The heat of fusion is hence calculated to be 5600 cal./mole.

For chromyl chloride, calculation of ΔH for $CrO_2Cl_2(l) \rightarrow CrO_2Cl_2(g)$ from the vapor pressure curve gives 8620 cal./mole. The Kistiakowsky equation gives 8040 cal./mole. The average of these two values is 8330 cal./mole. Since the vapor pressure curve shows a linear relation of log p versus $1/T$, the heat of vaporization does not change appreciably with temperature over the range 79° to 120°C.

F. VISCOSITY

There has been one published discussion of the viscosity of chromyl chloride, covering the range −5° to 70°C. (149). Values are given in table 3.

The extreme precision indicated by the published data is unwarranted, since qualitative observations show that the viscosity is affected markedly by purity, the purer samples generally having a lower viscosity. An independent unpublished measurement gives 0.80 centipoise at 28°C. (43).

The published results are shown to follow the Bachinskiĭ formula:

$$\eta_t = \frac{\eta_0}{1 + At + Bt^2}$$

where $A = 0.006807$ and $B = 0.000001188$.

The characteristics of the viscosity–temperature relationships for chromyl chloride, as compared to other inorganic liquids, are discussed in a subsequent paper (151).

TABLE 3

Viscosity of chromyl chloride

Temperature	Viscosity	Temperature	Viscosity
°C.	*poises*	*°C.*	*poises*
−5	0.01125	35	0.00830
0	0.01054	40	0.008070
5	0.01008	45	0.007855
10	0.009718	50	0.007660
15	0.009405	55	0.007492
20	0.009120	60	0.007348
25	0.008840	65	0.007230
30	0.008560	70	0.007129

G. SURFACE TENSION

No published data exist giving the surface tension of any chromyl compound. From the height of liquid in a capillary, the surface tension of chromyl chloride at 28°C. has been estimated in this laboratory as 37.2 dynes/cm. (43).

H. DIELECTRIC CONSTANT

Chromyl chloride is a poor ionizing solvent, having a low dielectric constant of 2.6 at 20°C. (252).

I. ELECTRICAL CONDUCTIVITY

It was early reported that chromyl chloride was a nonconductor of electricity (121). Recent unpublished work (43) gives an estimated specific conductivity of less than 10^{-10} mho, which was the sensitivity of the instrument used. In nitrobenzene, chromyl chloride appears to form polar addition compounds which give increased electrical conductivity (66).

J. INDEX OF REFRACTION

Because of the strong absorption of light by chromyl compounds, no published data are available on the index of refraction. Chromyl chloride does not transmit sodium light; hence measurements of n_D at this wavelength are impossible, and the high dispersion makes the use of the Abbé refractometer impractical. However, chromyl chloride does transmit light of the wavelength of the lithium line at 6708 A.; hence an approximate determination of the index of refraction can be made at this wavelength. The apparent index as measured with an Abbé refractometer in lithium light is 1.64 at 25°C., but because of high dispersion it is not feasible to correct this to give a value for n_D. Comparison with solids of known index gives an index between 1.667 (potassium iodide) and 1.678 (ammonium chlorostannate) (43).

K. PROPERTIES AS SOLVENT AND SOLUTE

Chromyl chloride again serves as the prototype of chromyl compounds, data on solvent properties being almost entirely lacking on other compounds of the group.

As solvent, chromyl chloride dissolves many halogenated organic solids and liquids, such as carbon tetrachloride, *s*-tetrachloroethane, and *p*-dichlorobenzene. It is also miscible with other covalent halides, such as stannic chloride. Hydrocarbons and oxygenated materials, such as benzene, hexane, and acetic acid, may mix with chromyl chloride, but the solutions are unstable because of reactions, often violent, between the components.

Qualitative measurements have been made of the solubility of various materials in chromyl chloride at room temperature (43). The results are given in table 4.

The most interesting property of chromyl chloride as a solvent is its ability to dissolve substantial amounts of chromium(VI) oxide. Heat is absorbed during the solution process. This property was suggested by study of dilute solutions of chromium(VI) oxide in chromyl chloride (10), which led to an ebullioscopic con-

TABLE 4

Solubility and reactivity of various substances in chromyl chloride

A. Liquids

Miscible; No Reaction	Miscible; Slow Reaction	Miscible; Rapid or Violent Reaction	Partly Miscible	Essentially Immiscible
CCl_4 CH_2ClCH_2Cl CH_2BrCH_2Br $SOCl_2$ $SnCl_4$ CH_3COCl CH_2Cl_2 $CHCl_2CHCl_2$ $CHCl_3$	$(CH_3CO)_2O$ CH_3COOH HNO_3, concentrated (100%) n-C_6H_{14} C_6H_6 Cyclohexane $C_6H_5NO_2$ CS_2	CH_3COBr $C_2H_4(COOC_2H_5)_2$ C_5H_5N S_2Cl_2 $C_6H_5CH_3$ $C_6H_4(CH_3)_2$ (*o*, *m*, *p*) *p*-Cymene $ClSO_3H$ (on heating) Oleum $C_6H_5NH_2$ *t*-Octylamine *t*-Butylamine $(CH_2CH_2OH)_3N$ Cyclohexylamine Dicyclohexylamine CH_3OH C_2H_5OH n-C_4H_9OH	Silicone 559 (slow reaction)	HCOOH (100%) H_2F_2 (100%) H_3PO_4 (85%) H_2SO_4 (70%) Hg

B. Solids

Excellent Solvent	Poor Solvent	Insoluble
Iodine (reacts) p-$C_6H_4Cl_2$ CrO_3 Naphthalene (reacts)	Phenol (surface reaction) Pentachlorophenol $AlCl_3$	$ZnCl_2$ $NaCrO_3Cl$ NaI $(NH_4)_2SnCl_6$ Na_2CrO_4 S (surface reaction) Metals, including sodium (surface reaction)

stant of 55. Other workers (118), observing the high solubility of chromium(VI) oxide at 180°C., believed that $Cr_2O_5Cl_2$ was formed. The solubility has been approximately investigated over a wide range of temperature with the following results:

Temperature	Chromium (VI) Oxide	Reference	Temperature	Chromium (VI) Oxide	Reference
°C.	*per cent*		*°C.*	*per cent*	
−40	10.0	(6)	25	15.6	(39)
0	10.7	(39)	25	18.9	(6)
0	13.8	(6)	180	39.2	(112)

The system apparently reaches equilibrium very slowly and the above data need confirmation. Infrared measurements appear to give some evidence of compound formation in this system (8).

The solvent behavior of the chromium(VI) oxide–chromyl chloride solutions is similar to that of the pure solvent. In some cases where chromyl chloride acts as an inert solvent, there is vigorous reaction with the chromium(VI) oxide solution. Examples are as follows (43): thionyl chloride forms brown, pasty solids; benzene and nitrobenzene are reduced to a black paste; hexane and carbon disulfide give a violent reaction.

Chromyl chloride also dissolves chlorine (205). This solubility has been measured and found to be, per formula weight of chromyl chloride:

At 0°C.

p (mm.)	753	824	923	984	1016	1051	1069	1101	1125	1150	1189	1198	1208	1302
Cl (gram-atoms)	0.68	0.78	0.91	1.00	1.04	1.12	1.16	1.20	1.25	1.30	1.35	1.40	1.43	1.70

Smoothed data for 760 mm.

Temperature (°C.)	0	−14	−21	−24
Cl (gram-atoms)	0.70	1.24	2.31	3.00

The solubility of chlorine in chromyl chloride has also been reported at many isolated pressures and temperatures, from atmospheric pressure to 1295 mm., and from 0° to −26°C. The solubility of chlorine in chromyl chloride is generally similar to that in sulfur monochloride; it is suggested that liquid chlorine and chromyl chloride may be completely miscible.

It has been reported (42) that solutions of chlorine in chromyl chloride become solid at room temperature, but this observation is probably based on the use of impure materials.

The effect of chromyl chloride as a solute has been employed as a means of determining the molecular weight of chromyl chloride (156, 169, 170, 171, 176). In almost all cases the molecular weight is greater than that calculated for CrO_2Cl_2 but less than that for a dimer, typical values being as shown in table 5.

It is typical of most experiments that the higher molecular weights are obtained at the lowest concentrations of chromyl chloride. Polymerization is suggested as a mechanism, but the other data available seem to argue against the existence of polymers of chromyl chloride. In stannic bromide the mechanism is apparently:

$$CrO_2Cl_2 + SnBr_4 \rightarrow CrO_2^{++} + SnBr_4Cl_2^{=}$$

In contrast, determinations of molecular weight by boiling-point measurements in carbon tetrachloride and carbon disulfide give normal values for the molecular weight (171). The data given in table 6 are listed (130).

TABLE 5

Molecular weight of chromyl chloride

Solvent	Molecular Weight	Reference	Solvent	Molecular Weight	Reference
Acetic acid	208–218	(156)	Benzene	165–175	(177)
	178–189	(169)			
Phosphorus oxychloride	159.3	(169)	Carbon tetrachloride	225–243	(177)
				222–273	(169)
Nitrobenzene	173–229	(169)			
Ethylene dibromide	178–399	(169)	Antimony pentachloride	193–215	(171)
$SO_3 \cdot POCl_3$	188–237	(176)	Stannic bromide	91.8–97.8	(171)

TABLE 6

Molecular weight of chromyl chloride by boiling-point measurements

Solution	*N*	$\Delta t/x$
	moles/1000 g. of solvent	
CrO_3 in chromyl chloride	0.05	35.4
	0.1	35.9
	0.15	36.5
	0.2	37.1
Chromyl chloride in carbon tetrachloride	0.1	28.9
	0.2	29.3
	0.3	29.7
Chromyl chloride in carbon disulfide	0.1	30.1
	0.2	29.5
	0.3	28.9
	0.4	28.3

It has been noted that chromyl nitrate dissolves chromium(VI) oxide, but the solubility is only slight (43).

L. PARACHOR AND STRUCTURE

Two measurements of the parachor of chromyl chloride have been made. Freiman and Sugden (74) give the following values:

Temperature	19°C.	41°C.	64°C.	78°C.
Parachor	36.61	34.55	32.16	30.48

The value for the parachor of chromium is taken as 54 units and it is inferred from the above results that chromyl chloride contains two semipolar bonds. Agarwal (2) was unable to measure the surface tension of chromyl chloride "due to excessive viscosity" and hence possessed an impure sample. He estimated the surface tension from the value in carbon tetrachloride solutions, assumed the presence of covalent bonding in his results, and ascribed to chromyl chloride a structure similar to that of sulfuryl chloride, SO_2Cl_2.

The dipole moment of chromyl chloride is very low (229) and this is confirmed by the low value of the dielectric constant (252). This indicates a fairly symmetrical arrangement of the molecule in which the bonds to oxygen and chlorine are approximately equivalent. This concept of the structure is further borne out by electron diffraction measurements (184) indicating the molecule to be a distorted tetrahedron with the measurements shown in table 7.

TABLE 7

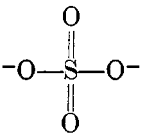
Bond lengths and bond angles in chromyl chloride

Bond	Bond Length	Bond Angle	Value
	A.		
Cr—O	1.57 ± 0.03	O—Cr—O	105°6′ ± 4°
Cr—Cl	2.12 ± 0.02	Cl—Cr—Cl	113°16′ ± 3°
Cl—O	3.03 ± 0.03	Cl—Cr—O	109°34′ ± 3°
Cl—Cl	3.54 ± 0.05		
O—O	2.49 ± 0.10		

There is a close analogy with sulfuryl chloride, for which the following data are reported (262):

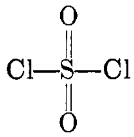
Bond	Bond Length	Bond Angle	Value
	A.		
S—O	1.43 ± 0.02	O—S—O	120° ± 5°
S—Cl	1.99 ± 0.02	Cl—S—Cl	111° ± 2°

Insufficient data are at hand to completely delineate the structure of either of these compounds. The tetrahedral arrangement and symmetry suggest sp^3 bonding in sulfuryl chloride and d^3s bonding in chromyl chloride. However, in sulfuryl chloride use of covalent radii as listed (261) leads to values of 2.03 A. for the sulfur–chlorine distance and 1.78 A. for the sulfur–oxygen distance. Use of the 0.87 "double-bond factor" gives a value of 1.54 A. In sulfates the bond distance is 1.51 A. and the best general structure for this ion is considered to be



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-}$$

with the possibility of several resonating forms. In sulfuryl chloride, by analogy, the structure



$$Cl-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl$$

is indicated, although the possibility of resonance seems minimized by the rather definite double-bond character of the sulfur–oxygen bond and the single-bond character of the sulfur–chlorine bond.

In chromyl chloride the ratio of the chromium–oxygen bond length to that of the chromium–chlorine bond length is 0.741, whereas in sulfuryl chloride it is 0.719. Since no compounds having a covalent chromium–chromium bond are known, the covalent radii for chromium are unknown. The ionic potential is 3.4 for Cr^{+6} and hence it yields covalent bonding. The difference between the chlorine and oxygen bond lengths for single covalent bonding should be 0.33; it is actually 0.55, whereas in sulfuryl chloride, which is known to have a double bond, it is 0.56. Hence chromyl chloride can be rather confidently stated to have a tetrahedral structure with double-bonded oxygen, similar to sulfuryl chloride.

Other chlorides of chromium are quite different. Chromium(III) chloride, $CrCl_3$, has a layer structure with chromium atoms occupying one-third of the octahedral holes in a cubic-close-packed chloride lattice. The chromium–chlorine distance is 2.38 A. (271). Chromium(II) chloride is probably ionic. Chromium(IV) chloride is stable only as a gas in equilibrium with chromium(III) chloride and chlorine at elevated temperatures, and its molecular structure is unknown.

Measurements of the absorption spectrum support the conclusion that chromyl chloride is chemically similar to the tetrahalides of Group IV elements and also indicate a distorted tetrahedral structure (143).

Recent calculations of orbital energies based on a tetrahedral structure show good agreement between calculated and observed absorption spectra in the visible and near ultraviolet (106). The first absorption is related to the dissociation of chromyl compounds, and the authors' calculations lead to the probability of the dissociation $CrO_2Cl_2 \rightarrow CrO_2 + Cl_2$ under the influence of light, which has been reported elsewhere in this review. The σ/π ratios for the bonding in chromyl chloride have also been calculated. These are 1.5 for chlorine and 0.73 for oxygen, somewhat lower figures than those calculated for sulfuryl chloride.

The observed solubility of chromium(VI) oxide in chromyl chloride is not unexpected, in view of the fact that it has recently been shown that chromium(VI) oxide likewise has a tetrahedral structure (22).

M. FLAME AND ABSORPTION SPECTRA

Early work was concerned with the spectrum of chromyl chloride in the gas flame. Introduction of chromyl chloride into the Bunsen flame produces a whitish violet luminous flame (197), in which Gottschalk and Drechsel (90) have identified some seventeen lines. The luminous flame is due to particles of chromium oxides produced by decomposition of the chromyl chloride. Since the compound decomposes in the flame, the spectrum observed cannot be attributed to chromyl chloride, but to its various decomposition products.

It has been reported that liquid chromyl chloride absorbs the entire visible spectrum (133). Such a conclusion is not in accord with the clear cherry-red color of pure chromyl chloride. Approximate measurements of the transmittance have been made on a filter photometer (43), with the results shown in table 8. For comparison, the transmittance of a chromium(VI) oxide solution having the same per cent transmission in the red (700 mμ) is also included.

TABLE 8

Absorption of light by liquid chromyl chloride

Cell length = 13 mm.

Nominal Wavelength of Filter	Per Cent Transmission	
	CrO_2Cl_2	CrO_3, 312 g./l.
mμ		
700	42	42
640	24	33
600	14	23
565	2	8
530	1	1
495	0	0
470	0	0
415	7	6

As has been previously noted, chromyl chloride does not transmit sodium light.

Investigation of the absorption of light by chromyl chloride both in the visible and the infrared, using a research spectrophotometer, should give an interesting insight into the structure of the compound.

The vapor possesses an extensive absorption spectrum and this has been widely investigated (152, 159). There are numerous bands in the orange, yellow, and green (232, 233, 234). Although Cornu (30) noted no regularity in the lines, others have attempted to classify their observations. The effect of temperature and pressure was studied on 103 lines between 5050 and 5894 A. (136), and these lines were further classified by the effect of such diluent gases as hydrogen, argon, nitrogen, sulfur hexafluoride, and carbon dioxide (137). Below 6000 A. and extending into the ultraviolet, diffuse absorption maxima without heads are repeated every 136 $cm.^{-1}$ These are interpreted (143) as evidence of the photochemical dissociation into chromium(IV) oxide and chlorine. The bands were further classified by other workers (187, 203). At low pressure and temperature, 58 lines were noted in the range 5000–5900 A. (101, 102); at 20°K., 9 bands in the range 5696–5791 A. (222). These bands were resolved and calculated to correspond to a dissociation energy of 1.35 kcal./mole.

At liquid air temperatures, lines corresponding to the nuclear quadrupole resonance of ^{35}Cl and ^{37}Cl were detected in the absorption spectrum of chromyl chloride and other volatile chlorides (40). The frequency corresponding to the ^{35}Cl resonance is 15.68 mc./sec.

The absorption spectrum of chromyl fluoride has been investigated in a three-prism apparatus (105). It is similar to that of chromyl chloride and suitable for examination by means of Condon curves.

IV. CHEMICAL PROPERTIES OF CHROMYL COMPOUNDS

A. STABILITY TOWARD HEAT AND LIGHT

Little information is available on the stability of chromyl compounds other than the chloride. The fluoride, if impure, polymerizes readily, the polymerization being accelerated by daylight or ultraviolet light (50). The pure fluoride, stored in darkness in aluminum phosphate glass or Kel-F, is stable for many months. The alleged polymer of chromyl fluoride is reported to be dirty white in color and to melt at about 200°C. (256). This statement is probably incorrect. No data are available on the thermal stability of the fluoride, but it would be expected to be slightly greater than that of the chloride.

Extensive work has been done on the chloride. The experience of the authors has been that chromyl chloride of technical purity (98 + per cent CrO_2Cl_2; small quantities of chlorine, sulfur trioxide, and chromium(VI) oxide) is entirely stable for an indefinite period when stored in either aluminum or stainless steel. In glass, the material is stable if protected from light. When exposed to light chromyl chloride deposits a black semisolid material on the glass which tends to shield the remainder from the action of light, and chlorine appears in the vapor phase. There is no significant increase in pressure because of the ready solubility of chlorine in chromyl chloride. This decomposition was observed by Étard (56), who postulated the reaction

$$CrO_2Cl_2 \rightarrow CrO_2 + Cl_2$$

and isolated chlorine from the decomposition products. Since the solid residue when dissolved in acid gave both trivalent and hexavalent chromium, its identity as chromium(IV) oxide was not established. According to others (170), after nineteen months exposure to light in a sealed container, a black amorphous deposit was formed, which fumed in air and had the odor of chromyl chloride. Analysis of this material showed a slightly higher chromium and lower chlorine content than chromyl chloride. The deposit was believed to be a solid polymer of CrO_2Cl_2 and $(CrO_2)_3Cl_2$, the latter compound having been reported as formed by heating chromyl chloride to 180–190°C. (244). The observations of East (43) suggest that the decomposition products are chlorine and a finely divided chromium(IV) oxide, which readily adsorbs large quantities of chromyl chloride, since analyses conforming to a definite composition were not obtained and chromyl chloride can be continuously removed by extraction. This adsorption mixture is also the material which is formed by chemical reduction of chromyl chloride and which has been responsible for the announcement of such "compounds" as $(CrO_2)_3Cl_2$ and $(CrO_2)_5Cl_6$.

This theory of the photochemical dissociation of chromyl chloride is supported by studies of the decomposition of the vapor under the influence of light. Decomposition takes place under the influence of wavelengths below 4200 A., giving chlorine with no change in pressure. Energy considerations show that light is absorbed and chlorine liberated (134, 135, 143). The photosensitivity of compounds of hexavalent chromium in mixture or combination with reducing agents is characteristic.

On heating, chromyl chloride is stable to 180°C. (43). Above 180°C. a dark decomposition product begins to form, which is apparently identical with that formed on photochemical decomposition (244). This loses adsorbed chromyl chloride on further heating and further decomposition occurs, until at 400°C. a magnetic oxide having the composition Cr_5O_9 results (230). Magnetic properties are also noted in the intermediate chromium oxide formed at 300°C. (266, 267, 268, 269, 270). On further heating, or on exposure of the vapor to a gas flame, Cr_2O_3 is formed (90, 163, 193, 194); a patent for making Cr_2O_3 depends on the pyrolysis of chromyl chloride vapor at 500–750°C. (192). Another patent (69) states that chromium may be deposited on metal surfaces by the pyrolysis of chromyl chloride, but this claim is probably incorrect.

Chromyl nitrate exhibits a slow decomposition at room temperature. This reaction is still under investigation, but the mechanism appears to be as follows: Chromyl nitrate, in its pure state, is in equilibrium with chromium(VI) oxide and dinitrogen pentoxide. However, dinitrogen pentoxide is known to decompose to dinitrogen tetroxide and oxygen and this reaction may be irreversible. There are two somewhat conflicting sets of data on this score. Daniels and Johnston

(38) have described the reaction as an irreversible first-order reaction, while information recently obtained on the analogous decomposition of fuming nitric acids indicates that an equilibrium pressure of decomposition products is eventually reached (138).

In the case of chromyl nitrate, there exists the possibility of the following reactions:

(1) $CrO_2(NO_3)_2 \rightleftharpoons CrO_3 + N_2O_5$

(2) $N_2O_5 \overset{?}{\rightleftharpoons} N_2O_4 + \frac{1}{2}O_2$

(3) $N_2O_4 + CrO_3 \xrightarrow{?} CrO_2 + N_2O_5$, or perhaps

(4) $2CrO_3 + 3N_2O_4 \xrightarrow{?} 2Cr(NO_3)_3$

Chromyl nitrate which has undergone decomposition contains a voluminous dark sludge which has not yet been identified. The pressure, in containers approximately half full of the liquid, increases linearly at the rate of 17 mm./day at 25°C. over a period of 90 days. The rate of decomposition, on a percentage basis, assuming reactions 1, 2, and 3, is thus 0.0194 per cent per day (144).

B. CORROSIVENESS AND ACTION ON METALS

There is very little published information on the action of chromyl compounds on metals.

Chromyl fluoride is described (256) as a strong fluorinating agent. It would thus be expected to react strongly with metals. However, later work (50) showed that the earlier product was contaminated with fluorine, and nothing has been reported on the action of pure chromyl fluoride on metals.

It has been reported (incorrectly) that chromyl chloride reacts violently with mercury (42, 253, 254). Others have used mercury for removing free chlorine from the liquid (169). The action of zinc or sodium on chromyl chloride vapor is reported to produce metallic chromium (68).

Extensive qualitative work has been done in this laboratory (43) on the corrosive action of chromyl chloride on a wide variety of metals. Those tested and the actions observed were as shown in table 9.

TABLE 9

Corrosive action of chromyl chloride on metals

Metal or Alloy	Action	Metal or Alloy	Action
Copper	No action	Cast iron	No action
Brass (70-30)	No action	Lead	No action
Aluminum, 14S	No action	Platinum	No action
Steel (SAE 1020)	Slightly etched	Sodium	Floats; forms coating of Na_2CrO_4, which stops reaction
Stainless steel 304	No action	Lithium	Same as sodium
Stainless steel 316	No action	Mercury	Yellow coating, no further reaction; reacts with chromyl chloride vapor above boiling point
Stainless steel 329	No action		
Stainless steel, Carpenter 20	No action		
Bronze	No action	Magnesium	No action
Monel	No action	Zinc	No action
Tin	Attacked; tin plate removed from tin can	Antimony	Corroded

TABLE 10

Corrosion of metals by chromyl chloride

Material	Duration of Test	Corrosion Rate by Weight Loss	
		mg./dm.^{2}*/day*	*in./yr.*
Aluminum 2S	86 days[*]	0.090	0.000048
Aluminum 2S	68 hours[‡]	1.6	0.00086
Aluminum 3S	86 days[*]	0.036	0.000019
Inconel	86 days[*]	0.036	0.0000061
Stainless steel 304	86 days[*]	0.054	0.0000099
Stainless steel 304	68 hours[‡]	8.7	0.0016
Stainless steel 316	86 days[*]	0.036	0.0000066
Stainless steel 316	68 hours[‡]	2.2	0.00040
Stainless steel 430	86 days[*]	0.054	0.000010
Hastelloy C	86 days[*]	0.018	0.0000029
Monel	86 days[*]	0.162	0.000026
Nichrome	86 days[*]	0.054	0.0000091
Stellite	52 days[*]	0.030[†]	—
Iron	68 hours[‡]	17.0	0.0031
Iron	98 days[§]	0.71	0.00013
Iron	98 days[¶]	0.050	0.0000091
Lead	68 hours[‡]	8.7	0.0011

[*] In the 86-day tests, the bulk of the corrosion took place in the first 8 days; corrosion after that time was negligible.

[†] Weight increase.

[‡] The 68-hr. tests were run on a different batch of chromyl chloride. The weight losses recorded were of the same order of magnitude as that observed after 8 days in the 86-day tests.

[§] This test was run on a third batch of material, sealed in air in a screw-top container with neoprene gasket.

[¶] Same chromyl chloride as in preceding note, but hermetically sealed in glass in dry nitrogen.

Quantitative corrosion tests (see table 10) have also been run on chromyl chloride with important metals (43, 91). All tests were at room temperature. There is reason to believe that the following figures may be considerably altered by changes in temperature or in the moisture, chlorine, or hydrogen chloride content of the chromyl chloride. The tests were run in sealed containers with approximately one-half of the specimen immersed in the liquid. In most cases, the liquid appears to be less corrosive than the vapor.

The data of table 10 further substantiate the chemical inertness of chromyl chloride to most metals, except the more electronegative metals whose chlorides are similar to chromyl chloride in properties. Stainless steel and aluminum are currently used for the shipment of chromyl chloride (27).

The corrosiveness of chromyl nitrate has been less thoroughly investigated but, like chromyl chloride, it appears to be inert to most common metals. As with nitric acid, however, the decomposition products are corrosive to stainless steel; aluminum is the preferred metal for use (43) if freedom from corrosion is the principal quality desired in a container.

C. ACTION ON NONMETALS

The literature record is again confined to chromyl chloride; even here, no information is available on the reaction between chromyl chloride and boron, silicon, germanium, arsenic, selenium, tellurium, or bromine.

Hydrogen reduces chromyl chloride at elevated temperatures, first to $Cr_2O_3 \cdot CrO_3$ and then to Cr_2O_3; hydrogen chloride is formed (215).

Carbon (charcoal) is not converted to phosgene when heated in chromyl chloride vapor; the products are Cr_2O_3 and $CrCl_3$ with oxides of carbon. If chlorine is mixed with the chromyl chloride, it is reported that pure chromic chloride is formed (174).

Carbon (graphite) reacts at room temperatures to form intercalary compounds containing 36.3–40.4 per cent CrO_2Cl_2. The interplanar spacing of the graphite is increased from 3.45 to 9 A. On heating to 200–300°C. the chromyl chloride is released and the graphite exfoliated to many times its original volume (32, 33). In liquid chromyl chloride the lattice is expanded 2.18-fold by the absorption of up to 51.2 per cent of chromyl chloride in the exfoliated product. Up to 23 per cent chromyl chloride is retained at 300°C. (212a).

Nitrogen does not react with chromyl chloride at temperatures below the boiling point (43).

Data on the reaction of phosphorus with chromyl chloride are contradictory. While some report that the phosphorus must be moist and that the vapor of chromyl chloride extinguishes burning phosphorus (241, 242, 243), others report an explosive reaction from adding phosphorus to chromyl chloride (253, 254). A check of this reaction indicated that white phosphorus, if clean, reacts vigorously with chromyl chloride; a flash and moderately sharp explosion occur. A coating of phosphorus pentoxide on the phosphorus may retard or prevent action (43).

Sulfur reacts with chromyl chloride with a hissing sound; the extent of the reaction depends on the fineness of division of the sulfur and the method of addition. A surface coating forms which stops further action. Chromyl chloride dropped on flowers of sulfur produces ignition, whereas powdered sulfur added slowly to the chloride reacts to produce a pink product which probably contains chromic chloride (43, 92, 93, 140) and chromic sulfate.

The action of fluorine on chromyl chloride at 200°C. in an alumina tube is reported to produce chromyl fluoride (256).

As previously stated, chlorine dissolves unchanged in chromyl chloride (205).

Iodine is reported to dissolve unchanged in chromyl chloride (253, 254), while McIvor (154) reports the formation of iodine chloride and the poorly characterized $(CrO_2)_3Cl_2$. A check of this experiment indicated a slow reaction (43).

D. OTHER INORGANIC REACTIONS

In general, the inorganic reactions of chromyl compounds are limited by the lack of solvency for most polar inorganic materials. The known reactions may be classified in four groups: hydrolysis, oxidation, formation of addition compounds, and miscellaneous reactions.

1. Hydrolysis

All chromyl compounds undergo hydrolysis, forming chromic acid and the acid of the negative group. These reactions are exothermic, but may take place slowly in cold water because of the insolubility of the chromyl compound. This is particularly true of chromyl chloride, which appears to be the most nonpolar; chromyl nitrate and fluoride are hydrolyzed more rapidly (42, 43, 248, 249, 253, 254). In the case of chromyl chloride the hydrolysis reaction may be followed by further action, giving chlorine and chromic salts (172).

$$2CrO_2Cl_2 + 3H_2O \rightarrow H_2Cr_2O_7 + 4HCl$$

$$H_2Cr_2O_7 + 12HCl \rightarrow 2CrCl_3 + 3Cl_2 + 7H_2O$$

2. Oxidation

The powerful oxidizing properties of chromyl chloride early received attention, one of the first reactions noted being that with ammonia, which proceeds with incandescence, even with concentrated aqueous solutions. It is variously listed that the products are CrO_3 (104), CrO_2 ($Cr_2O_3 \cdot CrO_3$) (201), and Cr_2O_3 plus CrN (220, 247), and that a volatile chromium compound is formed (147). In chloroform solution a brown precipitate results (104); Thomson (241, 242, 243) reported a brown mass. Most of these experiments were only qualitative in nature, and it is probable that the basic reaction is

$$2CrO_2Cl_2 + 6NH_3 \rightarrow 4NH_4Cl + Cr_2O_3 + N_2 + H_2O$$

similar to the decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

As in the case of ammonium dichromate, however, not all the nitrogen of the ammonia is evolved as the element. Traces of nitrogen oxides are formed, and some intermediate oxides of chromium result. This reaction should also receive further study to confirm or deny the reported formation of nitride.

Hydrogen sulfide passed into chromyl chloride is reported to precipitate Cr_2O_3 (140), while sulfur monochloride is likewise oxidized with hissing and incandescence to form a rose-colored powder, which presumably contains chromic chloride and chromic sulfate. Phosphorus trichloride and undiluted chromyl chloride react with explosive violence (158); phosphorus pentachloride yields phosphorus oxychloride, chromic chloride, and chlorine (218). Later, these reactions were studied by the use of carbon tetrachloride solutions of chromyl chloride. The results are described below.

Nitric oxide and carbon monoxide reduce chromyl chloride with the formation of a brown solid which was reported to be $(CrO_2)_5Cl_6$ (185). This product is reported to be similar to a mixture of CrO_2 and CrO_2Cl_2, but is magnetic. It has since been shown that chromium(IV) oxide is magnetic (4), and so the best interpretation of this reaction is probably that chromium(IV) oxide, adsorbing chromyl chloride, is formed. A further evidence of the strong adsorption is the reported insolubility of the "compound" in carbon disulfide (196). The compound $Cr_5Cl_5O_7 \cdot 2NO_2$ has also been reported from the action of nitric oxide on chromyl chloride but it has not been confirmed (240). By the action of nitrogen dioxide or the decomposition products of nitric acid on chromyl nitrate, a dark sludge is formed which may be anhydrous chromic nitrate, but is probably also chromium(IV) oxide (43).

Chromyl fluoride is reduced by arsenic trioxide, forming arsenic fluorides and chromic oxide (249).

3. Formation of addition compounds

Chromium(VI) oxide reportedly forms, with chromyl chloride at elevated temperatures, the compound $Cr_2O_5Cl_2$ (118). Repeated investigations of distillation fractions of chromium(VI) oxide–chromyl chloride solutions fail to give any evidence of such a combination (43), although infrared spectroscopy does give evidence of some compound formation in the solution (8). For the most part, these mixtures behave like simple solutions.

The formation of chlorochromates by the action of chromyl chloride on concentrated aqueous solutions of chromates is well known, and is in a sense a reaction of this type (223, 224). Fluorochromates are similarly formed from chromyl fluoride, although these compounds were originally reported as addition compounds such as $(NH_4)_2CrO_4 \cdot CrO_2F_2$ (250, 251).

Chromyl fluoride adds potassium fluoride and hydrogen fluoride to form the compound $CrO_2F_2 \cdot HF \cdot KF$, and this material is stable enough to provide a means for removing hydrogen fluoride from chromyl fluoride (50, 95).

Double salts of chromyl chloride with the alkali halides have been reported (260), but work in this laboratory has failed to disclose any chemical action or solubility (43). Even potassium iodide and ammonium iodide fail to be oxidized by chromyl chloride in the absence of water.

Reactions with the phosphorus halides have been quite extensively studied and represent both oxidation-reduction and addition reactions in most cases. The following compounds have been reported as obtained by the action of chromyl chloride on the halides indicated: $CrCl_3 \cdot PCl_5$ from phosphorus pentachloride (34, 35, 36, 257); $CrOCl \cdot POCl_3$ from phosphorus trichloride (78); $CrOCl \cdot POBr_3$ from phosphorus tribromide (78); $CrOCl \cdot PBr_3$ and other products from phosphorus pentabromide (79); $CrO_2Cl_2 \cdot PCl_5$ from phosphorus pentachloride (79); $CrO_2Cl_2 \cdot PI_3$ from phosphorus triiodide (79); $(CrO_2Cl_2)_2P_2I_4$ from P_2I_4 (79); a black substance, decomposing at 100°C., from phosphorus oxychloride (25).

The addition compounds were generally formed in carbon tetrachloride solution, while direct mixture of chromyl chloride with phosphorus trihalides led to violent reactions and decomposition (79).

4. Miscellaneous reactions

Chlorosulfonic acid and pyrosulfuric acid decompose chromyl chloride with formation of chromyl sulfate. The reaction is initiated by warming, and the liberated hydrogen chloride then reacts further to form chlorine and chromic salts (119, 120).

No chlorine is liberated when chromyl chloride is heated with urea (221). Instead, the urea is oxidized to nitrogen and carbon dioxide, with formation of chromic chloride and oxide.

Chromyl fluoride exchanges its fluorine with numerous metal oxides, forming boron trifluoride from boric oxide, silicon tetrafluoride from glass or silicon dioxide, and arsenic fluorides from arsenious oxide (248, 249).

E. THE ÉTARD REACTION

1. Introduction and history

The classical Étard reaction involves the addition of chromyl chloride to an organic molecule at one or more hydrogen atoms. This is followed by hydrolysis to yield aldehydes, ketones, and quinones. The typical example is the formation of benzaldehyde through the hydrolysis of the addition product of chromyl chloride with toluene. Chromyl fluoride (181) and chromyl nitrate (43) also can be used in this reaction. For purposes of this review, the Étard reaction may be defined as the addition of a chromyl compound to an organic molecule to form a separable addition product, followed by hydrolysis or alcoholysis to yield an oxidation product.

Alexander Leon Étard (1852–1910) had hardly reached his 25th year when he described the use of chromyl chloride in preparing benzaldehyde from toluene (59). Further contributions dealing with the reaction which was to bear his name followed in rapid succession (56, 57, 58, 61, 63, 64, 65, 66, 67), the work being substantially complete by the time Étard was 30 years of age. He determined the empirical composition of addition compounds and their decomposition products in a thorough manner. However, he did little to identify structures, because of the state of organic chemistry at that time. Isomeric compounds caused confusion. For instance, he reported nitrobenzoic acid as nitrotoluquinone. He did not know that cymene had an isopropyl group, nor the structure of the terpenes. Hence, although Étard's data are reliable, his conclusions bear reëxamination.

Others have continued Étard's studies, but Rohde (204) is the only worker who has prepared a comprehensive survey of the reaction since Étard's time. Rohde's work, published in 1901, contained much sound material, but his concept of the chromyl chloride addition compound was erroneous.

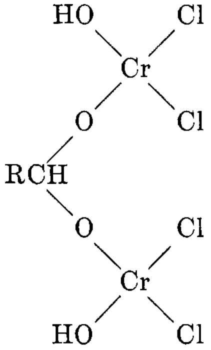
2. General nature of the Étard reaction

(a) Addition of chromyl chloride to organic molecules

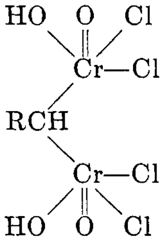
The Étard complex is formed by adding chromyl chloride, preferably in an inert solvent such as carbon disulfide or carbon tetrachloride, to an excess of the organic compound which also may be dissolved in the same solvent. The reaction is considered complete when a red color remains after the mixture has stood for 2 or 3 days. The insoluble complex is separated by filtration and washing.

Étard (60) controlled the reaction by diluting with carbon disulfide and cooling. Early work led him to believe that chlorination was involved in the reaction. Later he recognized that the intermediate was a true addition product and that chlorination was not an essential part of the reaction. Since that time numerous concepts of the addition complex have been advanced. These concepts must be examined for their ability to explain the following established facts:

(1) Usually two moles of the chromyl compound unite with one mole of the organic compound, with considerable evolution of heat and a change in color.
(2) Hydrolysis usually yields aldehydes and ketones, although chlorinated products, quinones, acids, and other products may be formed.
(3) On heating the complex, half the chlorine is driven off as hydrogen chloride.
(4) Certain materials, particularly nitro compounds, regenerate the original organic compound on hydrolysis.
(5) With some compounds, particularly terpenes, rearrangements of structure occur.
(6) Chromium(VI) possesses tetrahedral coördination.

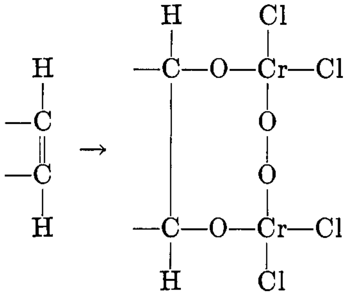


Étard, in 1881 (56), proposed the above structure for the adduct based on chromium(IV). This formula does not explain the regeneration of nitro compounds on hydrolysis. Furthermore, the concept of chromium(IV) in a stable solid form may be unacceptable. However, Westheimer and his coworkers have established the existence of intermediate valences as transition stages during chromic acid oxidations (263), and compounds of chromium(IV) and chromium(V) can exist in nonaqueous systems where the high free energy of formation of the hydrated chromium(III) ion cannot cause disproportionation of these valences. The heat effects and color changes also suggest the possibility of valence changes; however, this mechanism for adduct formation cannot be considered established.



In 1901 Rohde (204) suggested the above structure, involving a chromium–carbon linkage, and based the instability of the addition compound toward water on the existence of this bond. This formula is consistent with many reactions, but it is difficult to accept a coördination number of 5 for chromium(VI) in view of its well-established tetrahedral structure. Furthermore, chromyl chloride addition products are unlike the true chromium-organic compounds described by Hein (103), Fischer (70), and Zeiss (272), which have a π-electron bond or "sandwich" structure.

Other mechanisms have been proposed to account for specific addition reactions. Sword (237) suggested a peroxide link to describe addition at a double bond, thus:

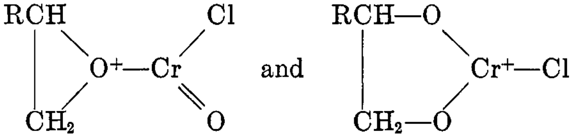


This structure appears unlikely in view of the extreme instability of known chromium peroxy compounds. In this addition reaction, also, chromyl chloride attaches to two separate carbon atoms.

Cristol and Eilar (31) studied the addition of chromyl chloride to olefins and found that the first mole added more rapidly than the second. They believed that only the first addition was significant, and postulated a mechanism similar to that frequently accepted for other additions to a double bond,

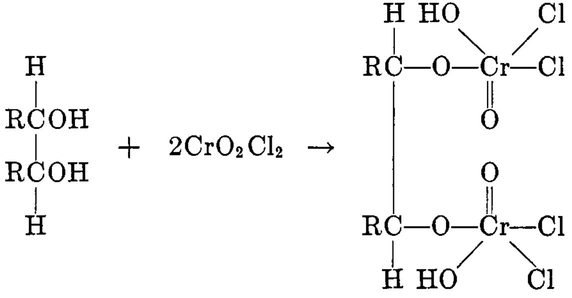
$$RCH{=}CH_2 \rightarrow [RCH{-}CH_2OCrOCl]^+ + Cl^- \rightarrow RCHClCH_2OCrOCl$$

where the intermediate ion may have the structures:

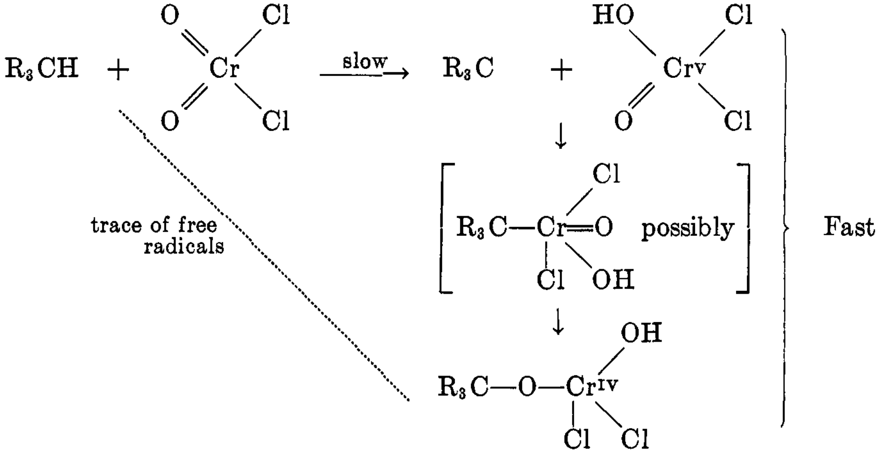


thus accounting for the isomerism noted by these workers. However, this mechanism, as in the case of Sword, is designed to explain special cases and cannot be applied to the Étard reaction in general.

Slack and Waters (226, 227) gave the following mechanism for the chromyl chloride addition to glycols:



thus explaining the cleavage to two aldehydes. Again the coördination of chromium is not taken into account, nor is this example illustrative of the more common types of Étard reaction. These investigators (86) also proposed a mechanism for oxidations with chromium(VI) oxide which may be adaptable to chromyl chloride. This adaptation is shown in the following sequence:

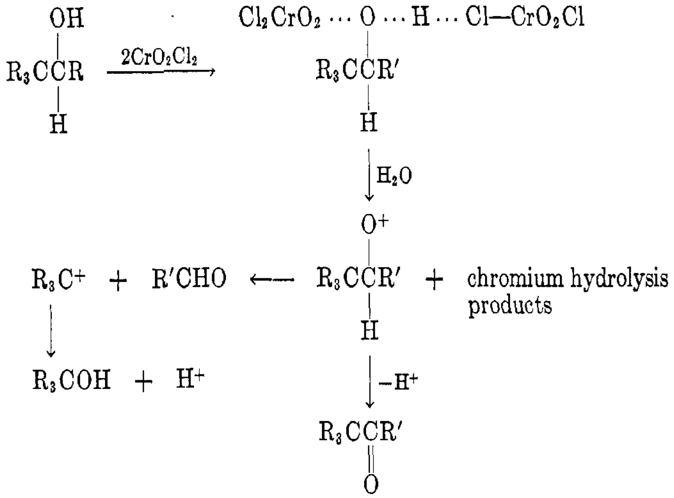


ending with a complex analogous to that proposed by Étard via a free-radical mechanism, and also suggesting Rohde's complex as a possible intermediate.

Hobbs and Houston (122) did not give a formula for the chromyl chloride addition products with various saturated hydrocarbons, but they assumed that carbonium-ion intermediates were formed on hydrolysis. From 2,2,4-trimethylpentane, for instance, the intermediate carbonium ion $(CH_3)_3CCH_2C^+(CH_3)$-CH_2OH was assumed to be formed.

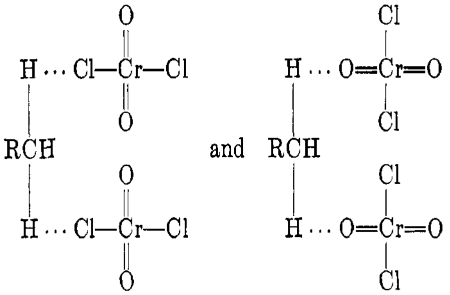
These workers and Crook (37) reported addition products with more than two moles of chromyl chloride per mole of hydrocarbon, particularly with long carbon chains as in *n*-hexane, 2,5-dimethylheptane, and 2,7-dimethyloctane. Two points of attachment are possible in such cases, and hydrolysis may be accompanied by rearrangements of great complexity. While these workers also noted that hydrocarbons having one or more tertiary hydrogens formed addition products more rapidly, it seems to the authors more likely that chain length is the determining factor in the formula of the addition complex. Some additional data are required here to establish definitely the formula of the addition product, since conclusions were based on analyses for chromium alone.

Mosher and coworkers (26, 173) have observed the cleavage of hindered secondary alcohols such as benzpinacolyl alcohol when treated with chromyl chloride in acetic anhydride and glacial acetic acid. This cleavage is not reduced in quantity by the presence of manganous ion and in some cases exceeds the 67 per cent which would be expected on the basis of Westheimer's hypothesis of penta- and tetravalent chromium. Hence a carbonium-ion mechanism is proposed to account for the observed results:



As the substituents are varied to yield R_3C groups having greater carbonium-ion stability, the amount of cleavage increases. The mechanism also agrees with the observed reduction in cleavage when pyridine or other Lewis bases are present.

The above work suggests another possible mechanism for the formation of chromyl chloride addition products, and this is the formation of a hydrogen bond. This mechanism preserves the tetrahedral coördination of chromium. Two types of hydrogen bond are possible:

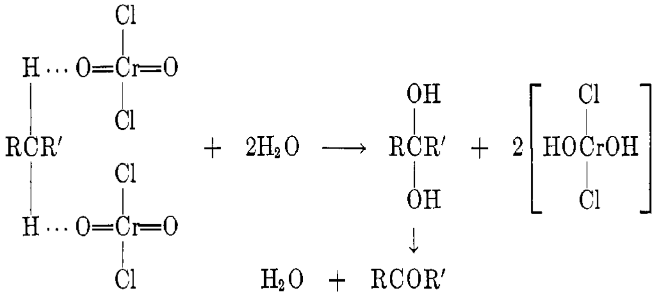


Both of these formulas afford an explanation of the regeneration of the original reagent which happens in some cases. The hydrogen-chlorine bond on first inspection gives a reasonable explanation of the loss of hydrogen chloride from the complex on heating, but further analysis of this mechanism shows that a carbon-chromium bond would form, and this appears unlikely. Because of the tetrahedral configuration of chromyl chloride, the more probable oxygen-hydrogen bond also provides an explanation of the evolution of hydrogen chloride, since it is possible for the hydrogen and chlorine to be in proximity. Hence the authors favor the second of the two formulas.

Both structures serve with equal facility to account for the observed products in the reaction of chromyl chloride with various organic materials. The principal objection to the hydrogen-bond formulas is the high heat of formation of the addition product, which is greater than that usually associated with this bonding. However, electron displacement during bond formation may cause the oxygen to assume a partial single-bond character and thus in effect produce chromium(V). Since hydrolysis of the complex usually results in products corresponding to chromium(IV), the roughly equal heat effects on complex formation and hydrolysis would be explained. However, no thermal measurements have been made, and these, plus magnetic measurements, must be made before a final conclusion can be drawn.

(b) Decomposition of the addition product

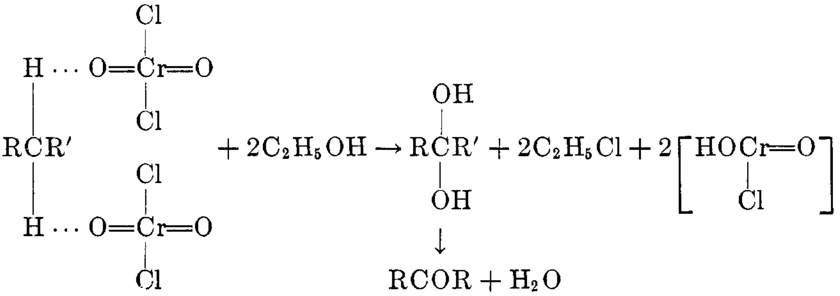
The Étard reaction is completed by hydrolysis of the addition product. The typical end result is the conversion of a methyl group to aldehyde, but this is obviously only a special case of a reaction where the compound RCH_2R' is converted to $RCOR'$. This hydrolysis (reaction I) is rapid and evolves considerable heat. To protect the organic product against the oxidizing action of the chromium(VI) liberated as a result of disproportionation of the chromium reduction products, sodium bisulfite may be added to the water. However, cold water in large excess usually is satisfactory.



The weight of evidence seems to indicate that the mechanism of formation of the oxidation product involves a carbonium ion. Dimers and other adducts which would result from a free-radical mechanism are lacking in the reaction products. The general nature of the carbonium-ion mechanism is shown in the discussion of the work of Celeste (26) above; for simplicity, only the end results will be shown in the reactions (I to XVIII) given in the text.

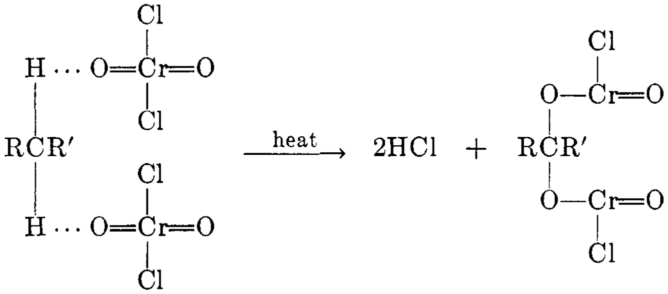
It will be noted that the chromium in this reaction ends as a compound of valence 4. Such compounds are, of course, unstable in aqueous solution and undergo disproportionation to yield chromic acid, chromic chloride, and other compounds of chromium(VI) and chromium(III). If the acidity, the concentration, or the temperature is sufficiently high, the chloride ion liberated may also react with chromium(VI) to form chromium(III) and chlorine. Since the end-products are complex and variable, they will not be shown in the formulas given.

Instead of water, alcohols may be employed (reaction II). Because of the lower acidity of the hydrolysis products when an alcohol is used, the likelihood of unwanted oxidation of the aldehyde is somewhat lessened. However, this advantage is slight. Étard also reported (56) that ethers reacted similarly, but Gibson, Robertson, and Sword (84) showed that ethyl ether carefully dried over sodium was without action.

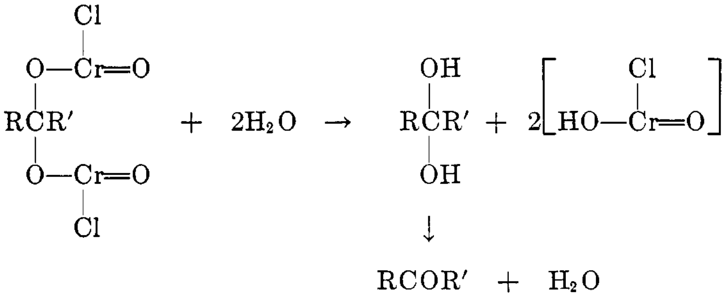


$$(\mathrm{H\cdots O{=}CrCl_2{=}O})_2\mathrm{RCR'} + 2C_2H_5OH \rightarrow \mathrm{RC(OH)_2R'} + 2C_2H_5Cl + 2\left[\mathrm{HOCr(Cl){=}O}\right] \quad \text{(II)}$$
$$\mathrm{RC(OH)_2R'} \rightarrow \mathrm{RCOR} + H_2O$$

If the addition compound is heated gently, half the chlorine is evolved as hydrogen chloride. As is characteristic of hydrogen bonds, the bond is broken by raising the temperature, and a compound of chromium(IV) is believed to be formed as shown in equation III. This thermal decomposition product on hydrolysis forms the same organic compound as is obtained by hydrolysis of the original addition compound (reaction IV).



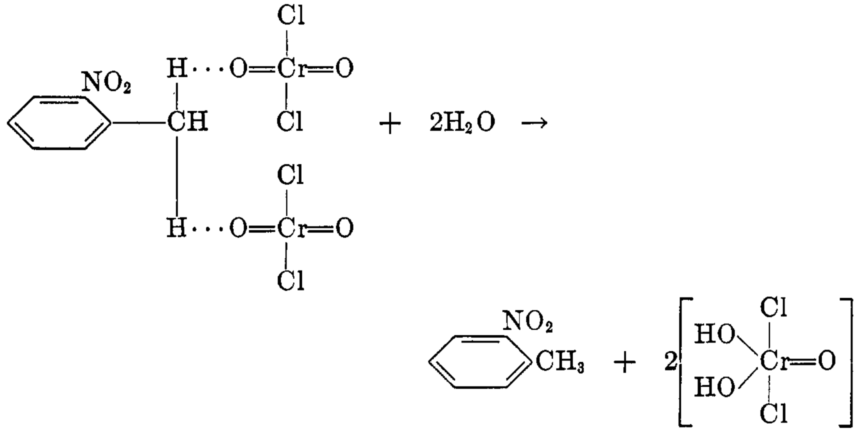
$$(\mathrm{H\cdots O{=}CrCl_2{=}O})_2\mathrm{RCR'} \xrightarrow{\text{heat}} 2HCl + (\mathrm{O{-}CrCl{=}O})_2\mathrm{RCR'} \quad \text{(III)}$$



$$(\mathrm{O{-}CrCl{=}O})_2\mathrm{RCR'} + 2H_2O \rightarrow \mathrm{RC(OH)_2R'} + 2\left[\mathrm{HO{-}CrCl{=}O}\right] \quad \text{(IV)}$$
$$\mathrm{RC(OH)_2R'} \rightarrow \mathrm{RCOR'} + H_2O$$

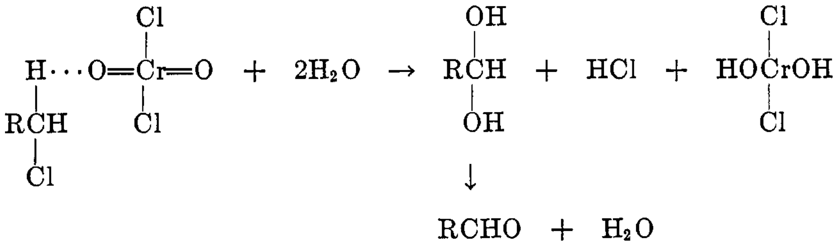
Heating the adduct, or its thermal decomposition product, above 250°C. results in chlorinated compounds and chromic chromates. Finally, above 1000°C. only chromium(III) oxide remains.

Substitution of electron-rich groups such as a nitro group, particularly in the ortho position as in *o*-nitrotoluene, weakens the bond and changes the electron pattern so that the addition product forms with difficulty, and the original substituted compound is regenerated on hydrolysis (reaction V). With dinitro compounds the bond is so weak that no chromyl chloride addition product separates.



(V)

With a monohalogenated methyl group, as in benzyl chloride, only one mole of chromyl chloride is added. Hydrolysis gives the aldehyde (reaction VI), the side-chain chlorine and the addition product both being hydrolyzed. Dihalogenated methyl groups, as in benzylidene chloride, do not add chromyl chloride.



$$\begin{array}{l}\mathrm{H\cdots O{=}\overset{Cl}{\underset{Cl}{Cr}}{=}O} \\ \quad\mathrm{|} \\ \mathrm{\underset{Cl}{RCH}}\end{array} + 2H_2O \rightarrow \mathrm{\overset{OH}{\underset{OH}{RCH}}} + HCl + \mathrm{HO\overset{Cl}{\underset{Cl}{Cr}}OH} \quad \text{(VI)}$$

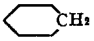
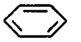
$$\mathrm{\overset{OH}{\underset{OH}{RCH}}} \downarrow \; RCHO + H_2O$$

Still another reason for accepting a hydrogen-bond formula is the fact that the ratio of two moles of chromyl chloride per mole of organic compound in the addition product is found almost without exception. This suggests strongly a uniform mechanism for adduct formation. However, this addition may occur in several ways, involving either the same carbon atom or two different carbon atoms. On decomposition of the addition product by hydrolysis, the net amount of oxidation accomplished may vary. This is shown in table 11, which lists several variations of the Étard reaction.

While the final average oxidation state of the chromium is more often 4 than any other value, the occasional occurrence of 3 and 5 as the final average valence state suggests that the same mechanism exists in all cases for the addition reaction, but that variations occur in the hydrolytic reaction to yield different valence states of the chromium. Hence the authors favor a hydrogen-bond formula for

TABLE 11

Variations of the Étard reaction

Starting Material	Product	Net Valence Change	Final Average Oxidation State of Cr*	Reaction
RCH_2R'	$RCOR'$	4	4	I
RCH_2CH_2R'	$RCHO + R'CHO$	6	3	XI
$RR'C(OH)C(OH)R''R'''$	$RR'CO + R''R'''CO$	2	5	XII
$RCH{=}CHR'$	$RCHO + R'CHO$	4	4	XVI
$RR'C{=}CH_2$	$RR'CO + CH_2O$	4	4	XIV
		4	4	I
		6	3	XVIII
RCH_2R'	$RCCl_2R'$	4	4	VII
$RCH{=}CH_2$	$RCHClCH_2OH$	2	5	XIII

* Based on a 2:1 CrO_2Cl_2 addition product.

the addition product, which gives a uniform mechanism for the addition and at the same time does not postulate a greatly reduced valence for the chromium. Thermal measurements would form an interesting test of this hypothesis, since it would be predicted that the heat of formation of the addition compound would be nearly the same in all cases, but that there would be considerable variation in the heat of hydrolysis, in which the major valence change occurs.

As the reactions shown in the above table are discussed in the following descriptions of individual Étard syntheses (Section IV,E,5), structural formulas for the hydrolysis will be presented to show how the hydrogen-bond formula fits the known facts.

(c) Choice of solvents

Glacial acetic acid: This diluent causes complicated reactions (23). The strongly oxidizing conditions convert the aldehyde to the corresponding acid, which may be condensed to an acid anhydride. In general, the presence of acetic acid detracts from the selectiveness of an Étard reaction; however, there are exceptions. For instance, in the cleavage of substituted glycols to aldehydes and ketones (reactions XVIII and XIX) high yields were obtained with a cooled acetic acid–carbon tetrachloride diluent (223, 227). Celeste (26) and Mosher, Celeste, and McGranaghan (173) also used this solvent in studying cleavage reactions.

Ethyl acetate: When used as a diluent, this solvent tends to be decomposed into acetic acid and aldehyde. Its use has no known advantage (18).

Carbon disulfide: Étard's use of carbon disulfide led to the aldehyde synthesis. An important consideration is that under atmospheric pressure the temperature of the reaction cannot rise above the boiling point of carbon disulfide (46°C.). Since chromyl chloride is not decomposed at this temperature, chlorination and other side reactions are reduced to a minimum. The chief disadvantage of carbon disulfide is its flammability; nor can it be used when chromic acid is dissolved in the chromyl chloride because of the violence of the reaction. Carbon disulfide should be dried before use in an Étard reaction. It has recently been brought to the attention of the authors (7) that a solution of chromyl chloride in carbon disulfide may decompose to some extent on standing for 24 hr.

Chloroform: Although chloroform is seldom employed as a diluent in an Étard reaction, it may be used with good results (56). There is no reaction with chromyl chloride below the boiling point of chloroform (61°C.).

Carbon tetrachloride: Because of its stability, carbon tetrachloride is ideal for reactions which are not critical below its boiling point (77°C.). Chromyl chloride and carbon tetrachloride are mutually soluble and nonreactive below 100°C. Proportions are not critical. Common proportions are three to five parts by weight of carbon tetrachloride per part of chromyl chloride and also per part of organic reactant. Before use the carbon tetrachloride should be thoroughly dried. It is not known if chromyl chloride addition products are as insoluble in carbon tetrachloride as they are in carbon disulfide. Carbon tetrachloride may be used in reactions containing glacial acetic acid or even free chromic acid.

(d) Effect of free chromium(VI) oxide

This oxide is readily soluble in chromyl chloride. Its presence increases reactivity, but possibly at the sacrifice of selectivity. As mentioned, this oxide may not be used with some diluents such as carbon disulfide; nor should the aldehyde synthesis (reaction I) be carried out in its presence because the corresponding organic acids may result. On the other hand there are reactions, such as the quinone synthesis (reaction XVIII), where the amount of oxygen consumed per mole of chromyl chloride in the addition product is double that of the ordinary reaction, and in these cases its introduction might be advantageous. Various cleavage reactions also have a high oxygen consumption and some of these reactions also might benefit from the addition of chromic acid to the diluent.

(e) Effect of free chlorine

In the Étard reaction the presence of free chlorine should be avoided; otherwise direct chlorinations may occur. Free chlorine was removed by Haller (98) by blowing the chromyl chloride with carbon dioxide before use. A better procedure is to reflux in a packed column, first sweeping out the column with dry nitrogen or other inert gas. Since chromyl chloride stored in the light decomposes with formation of chlorine (56), it is possible that the chromyl chloride used in some of the work reported below may not have been chlorine-free at the time of use, even though purified after preparation. Some of the chlorinations which have been reported as side reactions may have been due to chlorine in the chromyl chloride. Others may have resulted from the formation of chlorine from the chromium residues during hydrolysis. Other harmful impurities encountered in chromyl chloride are sulfate and moisture (175); however, impurities are very low in the chromyl chloride which is presently being made in this country.

3. Synthesis of aromatic aldehydes and ketones

(*a*) *From toluene:* The chief product is benzaldehyde (90 per cent); small amounts of benzoic acid, benzyl chloride, and benzylidene chloride are formed.

This is the prototype reaction first investigated by Étard (56). The general procedure used has been described, and the yields indicated above are obtained thereby. Reaction I is probably the only one occurring to any measurable extent.

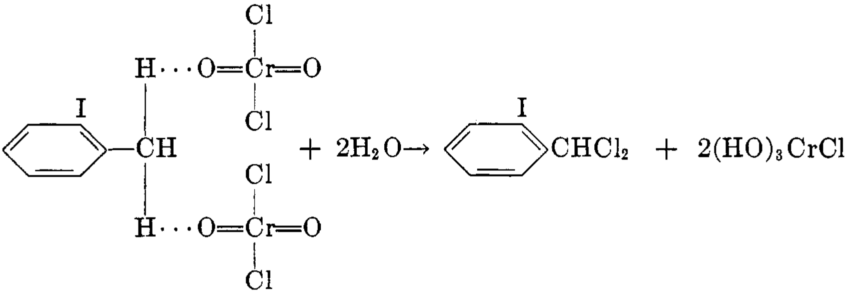
If the addition compound is heated at 240–250°C., half of the chlorine is driven off as hydrogen chloride (reaction III), leaving a residue having a composition corresponding to the formula $C_6H_5CH(CrO_2Cl)_2$. This product also can be decomposed by water or alcohol to form benzaldehyde (reaction IV).

By distilling the carbon disulfide from the filtrate from the adduct, a small amount of residual oil is obtained consisting chiefly of benzyl chloride. It also contains some benzylidene chloride. These probably result from accidental chlorination, perhaps due to photochemical decomposition of chromyl chloride during the several hours required for the reaction.

Carstanjen (24) found that no aldehyde resulted when toluene and chromyl chloride reacted in the presence of glacial acetic acid. This acid dissolved and decomposed the chromyl chloride addition product, splitting off acetyl chloride. Under these conditions the benzaldehyde was oxidized to benzoic acid, which was condensed to an acid anhydride. Other early investigators (204) reported the formation of complex chromic acetates, acetochromates, and chlorinated derivatives. It was the avoidance of a reactive polar diluent such as glacial acetic acid, coupled with the insolubility of the chromyl chloride addition compound in certain nonpolar solvents, that enabled Étard to obtain aldehydes.

(*b*) *From halogenated toluenes:* Although halogenation decreases reactivity, all monohalogenated toluenes react with two moles of chromyl chloride to form addition products. Decomposition may produce halogenated benzylidenes as well as aldehydes and small amounts of acids. Better yields of the aldehydes are obtained with *p*-halogenated toluenes than with *o*-halogenated. Likewise, better yields of aldehyde are obtained with chlorinated than with brominated toluenes.

The formation of the $CHCl_2$ group in the products, particularly when dealing with ortho substitution of a large halogen atom in the starting material, shows that a second mechanism is available for decomposition of the complex (reaction VII).



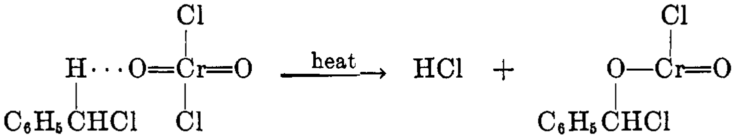
(VII)

The steric effects on this reaction are shown by the fact that reaction VII increases from para to meta to ortho, and from chlorine to bromine to iodine. For instance, with *o*-iodotoluene no aldehyde is obtained, the chief product being *o*-iodobenzylidene chloride.

Étard prepared *p*-bromobenzaldehyde by heating *p*-bromotoluene and chromyl chloride with a diluent. The addition product contained two moles of chromyl chloride per mole of bromotoluene, half the chlorine being evolved as hydrogen chloride (reaction III). The yield of aldehyde was low, the chief product being *p*-bromobenzoic acid (63). Stuart and Elliott (235), using 15–30 per cent solutions in carbon disulfide, reported yields up to 37 per cent of *o*-bromobenzaldehyde and *m*-bromobenzaldehyde, and also some of the corresponding benzylidene chlorides.

(*c*) *From benzyl chloride:* At first Étard thought that benzaldehyde was produced by way of benzyl chloride, but this is not the case. The reaction of chromyl chloride with benzyl chloride is slow; several days were required for an undiluted mixture of benzyl chloride and chromyl chloride to yield an adduct containing one mole of chromyl chloride per mole of benzyl chloride (56), or half the ratio in the ordinary addition product. On decomposition with water it gave a substantially theoretical yield of benzaldehyde (reaction VI). Traces of benzylidene chloride were formed by further chlorination, presumably in a manner analogous to the formation of benzyl chloride from toluene.

Heating the addition product in an oil bath at 170–180°C. for 1 hr. expelled hydrogen chloride (reaction VIII), leaving a residue corresponding to $C_6H_5CHCl(CrO_2Cl)$. Also there was formed an unidentified chlorinated oil which decomposed at 360°C.



$$\begin{array}{ll} & \quad\;\; \mathrm{Cl} \\ & \quad\;\; | \\ \mathrm{H}\cdots\mathrm{O}{=} & \!\!\mathrm{Cr}{=}\mathrm{O} \\ | & \quad\;\; | \\ \mathrm{C_6H_5CHCl} & \quad\;\; \mathrm{Cl} \end{array} \xrightarrow{\text{heat}} \mathrm{HCl} + \begin{array}{l} \quad\;\;\mathrm{Cl} \\ \quad\;\; | \\ \mathrm{O{-}Cr{=}O} \\ | \\ \mathrm{C_6H_5CHCl} \end{array} \qquad \text{(VIII)}$$

(*d*) *From nitrotoluenes:* No adduct is formed with the dinitrotoluenes. With a mixture of *o*- and *p*-nitrotoluenes, Étard (60, 61) obtained a two-mole chromyl chloride addition product by introducing chromyl chloride dropwise into a large excess of the nitrotoluenes heated to 150–200°C. without a diluent. This addition product was decomposed with water. No aldehyde resulted. Instead an alkali-soluble organic substance was obtained which on treatment with hydrochloric acid yielded shiny, brownish yellow flakes melting at 237°C. Étard thought that it was a nitrotoluquinone, $NO_2C_6H_2O_2CH_3$; however, von Richter (199) showed it to be *p*-nitrobenzoic acid. He also repeated Étard's work under milder oxidizing conditions. After standing for several days the customary brown addition product separated. On decomposition with water it gave the *p*-nitrobenzaldehyde in 70 per cent yield. There was also a trace of nitrobenzoic acid. Thus the normal chromyl chloride reaction (reaction I) occurred with a nitrotoluene substituted in the para position.

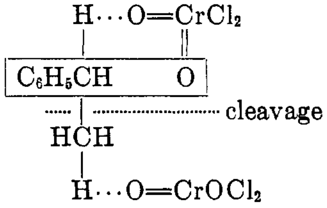
When the nitro group was in the ortho position, von Richter obtained a two-mole chromyl chloride addition product; however, on decomposition with water there was only a trace of the aldehyde. The bulk of the addition product reverted to *o*-nitrotoluene (reaction V).

Étard (64) reported that when a mixture of xylenes was used only the *p*-xylene reacted to produce *p*-tolualdehyde. Under milder conditions others (18, 258,

259) obtained 70–80 per cent yields of *o*-tolualdehyde and *m*-tolualdehyde from *o*-xylene and *m*-xylene. These yields are better than those reported from the use of oxidants such as lead dioxide, manganese dioxide, or persulfates (146). In the presence of glacial acetic acid, toluic acid and its anhydride were formed (23, 24).

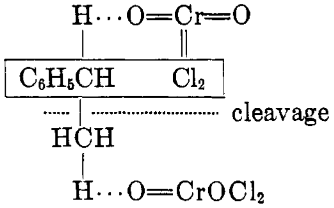
(*e*) *From mesitylene:* Mesitylene (9) undergoes a normal Étard reaction with one of its methyl groups (reaction I). This is a preferred method for the preparation of mesitylenaldehyde (146). Higher methylated homologs also react; if unsymmetrical they yield mixed aldehydes. In the presence of glacial acetic acid, mesitylenic acid was reported to be formed (24).

(*f*) *From ethylbenzene:* Étard, and later von Miller and Rohde (160), showed that two moles of chromyl chloride combined with one mole of ethylbenzene. This occurred in three ways: (*1*) both chromyl groups attached to the CH_3; (*2*) both groups attached to the CH_2; (*3*) one group attached to the CH_3 and the other to the CH_2. The first attachment predominated, yielding phenylacetaldehyde. Attachment of both chromyl groups to the CH_2 yielded acetophenone. Both these syntheses are examples of the Étard reaction by means of which CH_2 is oxidized to CO (reaction I). The formation of benzaldehyde is more involved. Here the attachment of chromyl chloride to adjacent carbon atoms results in cleavage (reaction IX). Formation of benzylidene chloride may be explained as a combination of reactions IX, VII, and X. Traces of chloroacetophenone may be due to chlorination combined with the ketone synthesis (reaction I).



$$\begin{array}{l} \mathrm{H}\cdots\mathrm{O{=}CrCl_2} \\ \quad | \qquad\quad \| \\ \boxed{\mathrm{C_6H_5CH} \quad \mathrm{O}} \\ \cdots | \cdots\cdots\cdots \text{cleavage} \\ \mathrm{HCH} \\ \quad | \\ \mathrm{H}\cdots\mathrm{O{=}CrOCl_2} \end{array}$$

(IX)



$$\begin{array}{l} \mathrm{H}\cdots\mathrm{O{=}Cr{=}O} \\ \quad | \qquad\quad \| \\ \boxed{\mathrm{C_6H_5CH} \quad \mathrm{Cl_2}} \\ \cdots | \cdots\cdots\cdots \text{cleavage} \\ \mathrm{HCH} \\ \quad | \\ \mathrm{H}\cdots\mathrm{O{=}CrOCl_2} \end{array}$$

(X)

(*g*) *From diethylbenzene:* Two moles of chromyl chloride react with one of diethylbenzene to form an adduct which on decomposition with water yields a number of unidentified aldehydes and ketones (56). The diethylbenzene isomer was unspecified, and the product may have been a mixture of isomers.

(*h*) *From propylbenzene:* The customary two-mole chromyl chloride addition product with propylbenzene was considered by Étard (56) to yield hydrocinnamaldehyde, $C_6H_5CH_2CH_2CHO$, on decomposition with water. Dollfus (41) and von Miller and Rohde (160) showed that the chief products were benzyl methyl ketone and benzaldehyde, together with some benzylidene chloride and unidentified chloroketones. This indicated that chromyl chloride attached simultaneously to both CH_2 groups, preference being for the CH_2 adjoining the CH_3. Attachment of both chromyl groups to the other CH_2 was difficult, only traces of propiophenone being formed. The formation of benzyl methyl ketone was analogous to that for acetophenone (reaction I). Propiophenone was formed in the same general manner. The cleavage of propylbenzene to form benzaldehyde was analogous to the cleavage of ethylbenzene (reaction IX). Likewise benzylidene chloride was formed in the same way as from ethylbenzene (reaction X).

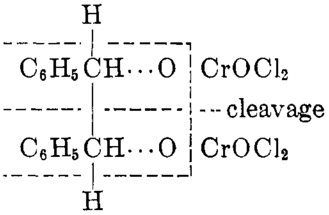
(*i*) *From cumene:* Chromyl chloride combines with cumene, $C_6H_5CH(CH_3)_2$, to form a 2:1 adduct which on hydrolysis yields chiefly hydratropaldehyde and acetophenone (161). From this it is apparent that there was no simultaneous attachment to different methyl groups. Hydratropaldehyde forms in the same way that benzaldehyde was derived from toluene (reaction I). A better yield of aldehyde was obtained using chromyl chloride than with other oxidants (146). Acetophenone resulted from attachment to adjacent carbon atoms followed by cleavage (reaction IX).

(*j*) *From cymene:* Chromyl chloride attaches to cymene, $p\text{-}CH_3C_6H_4CH(CH_3)_2$, in a manner analogous to its reaction with cumene. There is no attachment to the lone methyl group. von Miller and Rohde (160, 161) obtained a two-mole chromyl chloride addition product by the reaction of 10 per cent solutions of cymene and chromyl chloride in carbon disulfide. On decomposition of this product with water the chief products were identified as *p*-tolyl methyl ketone and *p*-methylhydratropaldehyde (reaction I). Contrary to Étard's opinion, there was no formation of cumaldehyde, $p\text{-}CHOC_6H_4CH(CH_3)_2$. Similar results have been reported by others (54, 146, 186, 200). The corresponding meta aldehydes and ketones have been obtained with *m*-cymene (139), but yields were low because of a tendency for *m*-methylhydratropaldehyde to undergo resinification, and for *m*-tolyl methyl ketone to undergo chlorination. The meta ketone was identified by its haylike odor. Little is known about the reaction of chromyl chloride with *o*-cymene. The above work on cymenes has been reviewed (204).

(*k*) *From p-amylmethylbenzene:* Étard (65) reported a normal reaction of $p\text{-}CH_3C_6H_4C_5H_{11}$ with chromyl chloride but did not identify the hydrolysis products.

(*l*) *From bitolyls and biphenyl:* Weiler (258, 259) reported the customary two-mole chromyl chloride addition product with *p,p'*-bitolyl. On decomposition with water there resulted a small amount of *p*-(*p'*-tolyl)benzaldehyde. This is another example of the direct aldehyde synthesis (reaction I); however, the main product was an unidentified brown resin. There is no account of the formation of an adduct with biphenyl. Carstanjen (24), employing a solution of biphenyl in glacial acetic acid, reported the formation of benzoic acid, presumably by rupture of some of the benzene rings.

(*m*) *From bibenzyl:* The wide variety of products reported in the Étard oxidation of bibenzyl bespeaks a variety of points or manner of attachment. The principal product reported (258) is benzaldehyde, formed by a cleavage-oxidation in which a mole of chromyl chloride attaches to each CH_2 group. The hydrolysis should yield trivalent chromium (reaction XI). Desoxybenzoin forms through a normal reaction (reaction I). Benzil and benzoin must result from the further addition of chromyl chloride, because of the valence changes involved. The reported presence of benzophenone is perhaps due to the presence of a small amount of 1,1-diphenylethane present in the starting material, although it is possible that it is formed through a pinacol rearrangement. Minor amounts of benzophenone, benzoic acid, benzyl chloride, and benzylidene chloride are also formed.



$$\begin{array}{l} \qquad\quad H \\ C_6H_5CH\cdots O \mid CrOCl_2 \\ \qquad\quad \mid \qquad\quad\ \mid \text{-- cleavage} \\ C_6H_5CH\cdots O \mid CrOCl_2 \\ \qquad\quad H \end{array} \qquad (XI)$$

(*n*) *From diphenylmethane and triphenylmethane:* Two moles of chromyl chloride attach solely to the methylene group of diphenylmethane with the result that an almost quantitative yield of benzophenone is obtained (258) (reaction I). Triphenylmethane, dissolved in carbon tetrachloride, gave only a one-mole chromyl chloride addition product, $(C_6H_5)_3CH(CrO_2Cl_2)$, a result which would be expected (215, 216). Its hydrolysis products were not reported; the work of Celeste (26) suggests that triphenylcarbinol forms and is possibly converted to triphenylmethyl chloride. An attempt by one of the authors (H.) to obtain triphenylmethyl chromate by the action of chromyl chloride on triphenylcarbinol led to a quantitative yield of triphenylmethyl chloride.

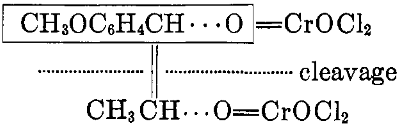
(*o*) *From p-benzyltoluene:* The customary two-mole chromyl chloride adduct formed with p-$C_6H_5CH_2C_6H_4CH_3$. On decomposition with water there was a 62 per cent yield of phenyl *p*-tolyl ketone, again indicating that the chromyl group prefers attachment to the methylene group (258). Also formed were small amounts of *p*-benzylbenzaldehyde. Both of these products derive from the normal reaction (reaction I). Derivatives of the benzylidene chloride type, and an unidentified acid, presumably benzylbenzoic, were also formed in small amounts.

(*p*) *From butyrophenone:* A chloroform solution of $C_6H_5COC_3H_7$ yielded with chromyl chloride (14) a two-mole addition product. On decomposition with water the chief product was benzoylpropionaldehyde (reaction I). Reduction with sodium amalgam gave the glycol, $C_6H_5CHOH(CH_2)_2CH_2OH$. A small amount of the butyrophenone was regenerated (reaction V).

(*q*) *From acetophenone:* In the same manner, a two-mole chromyl chloride adduct formed with acetophenone (21). On hydrolysis a small amount of benzoylformaldehyde, C_6H_5COCHO, appeared to be formed but was not fully identified. Most of the acetophenone was regenerated (reaction V). It is interesting that chromyl chloride reacted better with butyrophenone.

(*r*) *From nitrogen bases:* Most attempts to produce aldehydes of nitrogen bases by means of the chromyl chloride reaction have been unsuccessful. The ring nitrogen of heterocyclic compounds is oxidized. Pyridine is violently attacked by chromyl chloride. No aldehydes were obtained from the reaction of substituted quinolines with chromyl chloride (100). Carstanjen (23, 24) reported that chromyl chloride reacted with aniline in the presence of glacial acetic acid to yield a "quinone." Einhorn (48) obtained a well-crystallized trimethylquinoline aldehyde hydrate, $C_{13}H_{13}NO \cdot 3H_2O$, from the reaction of chromyl chloride with a tetramethylquinoline, but did not report the orientation of the methyl groups. This reaction may be similar to the ordinary oxidation (reaction I).

(*s*) *From anethole:* Étard (63) reported, without giving details, that anethole combined with chromyl chloride, yielding anisaldehyde on hydrolysis. The formation of anisaldehyde (reaction XII) may be explained by the attachment of a mole of chromyl chloride on each side of the double bond, followed by an aldehyde cleavage analogous to that of ethylbenzene (reaction X). Similar double-bond attachments of chromyl chloride occur with alkenes and other unsaturated compounds such as styrene and stilbene.



$$\begin{array}{c} \boxed{CH_3OC_6H_4CH\cdots O}{=}CrOCl_2 \\ \cdots\cdots\cdots \Vert \cdots\cdots\cdots\ \text{cleavage} \\ CH_3CH\cdots O{=}CrOCl_2 \end{array} \qquad \text{(XII)}$$

(*t*) *From 4-methoxy-2-nitrotoluene:* A 50 per cent yield of 2-nitroanisaldehyde (17) was obtained from 4-methoxy-2-nitrotoluene, according to the normal Étard reaction (reaction I).

(*u*) *From nitromethylbiphenyls:* Oxidation of 4-methyl-4′-nitrobiphenyl and 4-methyl-2′-nitrobiphenyl gave moderately good yields of the corresponding 4-aldehydes (94) according to the normal Étard reaction (reaction I).

(*v*) *From sterols:* Patents have been issued for the preparation of chromyl chloride complexes of sterols and their degradation products (211, 212). In typical examples cholesterol dibromide yielded progesterone, and cholesterol acetate dibromide gave pregnenolone acetate.

4. Reactions with terpenes

Two moles of chromyl chloride attach to a terpene. Usually the addition takes place at a double bond, preferably one outside the nucleus. This is presumed to make the terpene likely to undergo rearrangement (237), and there is evidence to show that such rearrangements occur if no such hydrogens are available for addition. While work on this subject is voluminous, most of that done by the early investigators must be discarded because they did not identify the starting hydrocarbons—much less the derived products. Shortly before the turn of the century, the relation of the terpenes to cymene was clarified by the brilliant work of Italian and German investigators. The section on cymene should be read before proceeding further, because many of the Étard reactions with terpenes result in dehydrogenation and rearrangement to form cymene derivatives.

The tendency of terpenes to undergo rearrangement by a carbonium-ion mechanism, particularly in the presence of hydrogen ion, is well known. Since chromyl chloride may be considered to be a Lewis acid, and since the hydrolysis products are acidic, it is not surprising that rearrangements occur when the Étard reaction is applied to terpenes. It has not been determined whether the rearrangement occurs at the time of formation of the chromyl chloride adduct, or during its hydrolysis. The former mechanism may be more likely in the case of the pinenes, and the latter in the oxidation of camphenes and bornylenes.

The nomenclature of terpenes is complex and has but recently been systematized (3). The "terpene names" are used in this paper, but the equivalent names as derivatives of the eight fundamental ring structures are given in the cited references. The thujane and *p*-menthane ring systems, having an isopropyl group para to a methyl group on a six-membered ring, are particularly likely to behave like cymene with chromyl chloride.

(*a*) *With α-pinene:* The reaction of chromyl chloride with α-pinene in carbon disulfide solution produced a voluminous precipitate having a composition corresponding to the formula $C_{10}H_{16}(CrO_2Cl_2)_2$ (116). When added to cold water it decomposed with evolution of heat and the formation of a dark heavy oily product which, on ether extraction, washing with alkali, and drying, yielded a transparent brown oil with a strong aromatic odor. This oil formed an addition product with sodium bisulfite. On heating it decomposed, giving off heavy white fumes and leaving a black resinous mass. On steam distillation it yielded a clear yellow oil having the same aromatic odor as before distillation. Analysis of this oil corresponded to the formula $C_{20}H_{33}OCl$. Under diminished pressure it distilled within a five-degree range without changing its appearance, its odor, or its behavior toward sodium bisulfite. However, analysis indicated loss of one mole of water. Further work (112) showed it to contain a saturated aldehyde, an unsaturated ketone, and a chlorinated oil. While derivatives of these compounds were prepared, their constitution was not established. Okuda (178, 179, 180) obtained by steam distillation a plentiful yield of an oil containing 7.5 per cent of isocamphenilanaldehyde but the principal constituent was *d*-pinocamphone.

(*b*) *With β-pinene:* Some time after the work with α-pinene (112, 116) the reaction of chromyl chloride with β-pinene was investigated by the same laboratory (110). This pinene formed a two-mole chromyl chloride addition product, $C_{10}H_{16}(CrO_2Cl_2)_2$. On hydrolysis it gave the same unsaturated ketone as was obtained from α-pinene; however, other products were different, consisting of an optically inactive *trans*-pinol glycol, two unidentified aldehydes, and resinous material. No chlorinated compounds were noted similar to those obtained from α-pinene. β-Pinene again possesses a structure to which chromyl chloride cannot become attached without rearrangement.

(*c*) *With camphene:* Étard (56) reported a two-mole chromyl chloride addition product which on decomposition with water gave an aldehyde which he thought was camphenaldehyde, $C_{10}H_{14}O$. Bredt and Jagelki (19) claimed the product to be camphenilanaldehyde, $C_{10}H_{16}O$, but they assigned to their "camphene" the structure now assigned to bornylene. Inasmuch as bornylene is known to yield camphenilanaldehyde, the data on camphene require reëvaluation with starting materials properly characterized. The well-known rearrangement of camphene to form bornyl chloride with hydrogen chloride may play a part in the formation of the camphenilanaldehydes.

(*d*) *With bornylene:* A two-mole chromyl chloride addition product was formed which underwent internal rearrangement to yield chiefly camphenilanaldehyde (113). Today this reaction is a textbook example (264). In addition a chlorocamphor, $C_{10}H_{15}OCl$, has been reported.

(*e*) *With limonene:* The major effect of chromyl chloride is to transform limonene to cymene, to whose isopropyl group it attaches as described for cumene. There is only a trace of direct addition of chromyl chloride to the methyl group. A two-mole chromyl chloride addition product formed with limonene. Unlike the addition products with pinene, camphene, and bornylene, it was a cymene derivative containing two less hydrogens. The chief products on decomposition by water were the same as from cymene: *p*-tolyl methyl ketone and *p*-methylhydratropaldehyde. Some cymene was also found in the end product. Yields were low owing to the formation of resinous matter (108). Unidentified aldehydes and ketones also have been reported (107).

(*f*) *With α-terpinene:* As in the case of limonene, the two-mole chromyl chloride addition product with α-terpinene underwent a cymene transformation. However, the yield of hydrolysis products was better, consisting chiefly of *p*-methylhydratropaldehyde and *p*-tolyl methyl ketone. Also reported was an unidentified ketone having a peppermint odor, perhaps a hydrotolyl methyl ketone, *p*-$CH_3C_6H_6COCH_3$, resulting from the direct addition of chromyl chloride without a cymene transformation (108).

(*g*) *With sabinene:* At first (115) the Étard reaction with sabinene was thought to produce 4-isopropylidenecyclohexanone, $(CH_3)_2{=}\underline{CCH_2CH_2COCH_2CH_2}$. Later work (114) identified the chief product as *p*-tolyl methyl ketone, thus establishing that this terpene underwent a cymene transformation in the same general manner as limonene and α-terpinene. Since sabinene is a thujane derivative, it is not surprising that it gives cymene products.

(*h*) *With sesquiterpenes:* The action of chromyl chloride on the sesquiterpenes has been investigated (84). The complex with β-caryophyllene was reported to contain slightly more chromium than required for the customary two-mole addition product. The investigators suggested either the splitting of hydrogen chloride from the addition product or the presence of a three-mole addition product. Similar addition products were formed with cadinene and cedrene. On hydrolysis the sesquiterpene addition products yielded no aldehydes. The chief products were as follows:

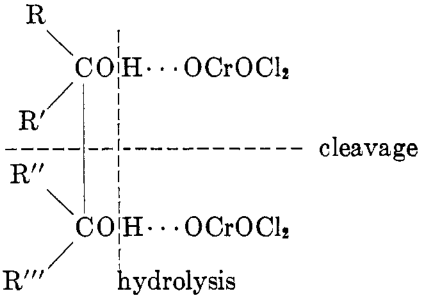
From β-Caryophyllene	From Cadinene	From Cedrene
Caryophyllene alcohol Chlorinated substances $C_{15}H_{24}O$, an unidentified ketone $C_{15}H_{20}O_2$, an unsaturated ketone	Organic acid (trace) $C_{15}H_{24}O$, a neutral volatile liquid which yielded no semicarbazone; probably the same product as was obtained by oxidation with chromium(VI) oxide	Chlorinated substances $C_{15}H_{24}O$, an unidentified ketone which yielded a semicarbazone

(*i*) *With natural rubber:* A preliminary publication states that chromyl chloride forms definite addition compounds with natural rubber, analogous to those with the terpenes (231).

5. *Oxidation of substituted glycols*

With substituted glycols of the type RCHOHCHOHR′ the Étard reaction results in cleavage to form two aldehydes, whereas glycols of the type RR′C(OH)C(OH)R″R‴ form two ketones. The reaction in each case is similar (reaction XII).

(*a*) *Hydrobenzoin:* Hydrobenzoin reacted with chromyl chloride in a cooled acetic acid–carbon tetrachloride solution to form a two-mole addition product, $(C_6H_5CHOH)_2(CrO_2Cl_2)_2$, which on hydrolysis split into two moles of benzaldehyde (reaction XII). The yield was 91 per cent (226, 227). The attachment of the chromyl chloride was to the hydroxyl hydrogens because the behavior is the same when the other hydrogen of the secondary alcohol groups is replaced. Note that there is no evidence here of the rearrangement to form diphenylacetaldehyde, which would yield benzophenone as a product. (See the sections on bibenzyl and bornylene, pp. 38 and 42.)



(XII)

(*b*) *Pinacol:* By reaction XII, a 71 per cent yield of acetone was obtained (226, 227).

(*c*) *Benzopinacol:* In like manner (reaction XII) benzopinacol formed with chromyl chloride a two-mole addition product, $[(C_6H_5)_2COH]_2(CrO_2Cl_2)_2$, which on decomposition by water split into two moles of benzophenone. The yield was 81 per cent (226, 227).

6. *Cleavage reactions of hindered secondary alcohols*

Mosher and his students have studied in detail the oxidation and cleavage of various hindered secondary alcohols by the action of chromyl chloride (26, 173). The secondary alcohols employed are closely related to the pinacols described in Section IV,E,5, since they are derived from them by rearrangement and reduction. For the most part, these experiments were performed in acetic acid–acetic anhydride solutions, the oxidant solution being added dropwise or by pouring. The reaction mixture was then hydrolyzed and separated without isolation of the chromyl chloride adduct in most cases. Aldehydic products were usually identified and weighed as the 2,4-dinitrophenylhydrazones.

(*a*) *Benzpinacolyl alcohol:* In benzene solution, the reaction proceeds about equally to give β-benzpinacolone by the normal Étard reaction, and to give benzaldehyde and triphenylcarbinol by cleavage, the former reaction predominating. In ether and acetic acid–acetic anhydride, cleavage proceeds to the extent of 100 per cent, no β-benzpinacolone being recovered. There is a slight amount of retropinacolone rearrangement to form tetraphenylethylene in some experiments. The speed of addition of the chromyl chloride had no effect on the distribution of the products. When pyridine, a Lewis base, is added to the mixture, the amount of cleavage is reduced drastically, being reduced to 8 per cent when 0.127 mole of pyridine is used for each 0.01 mole of benzpinacolyl alcohol. As would be expected from the description given above of the action of chromyl chloride on pyridine, the pyridine must be added to the alcohol–solvent mixture and cannot be used as a solvent for the reaction. Unlike Westheimer's experience, the addition of manganous salts is without effect on the cleavage (26). The chromyl chloride adduct was isolated by carrying out the reaction in carbon tetrachloride, and found to have the usual 2:1 mole ratio.

(*b*) *Pinacolyl alcohol:* With pinacolyl alcohol, in which the trimethylmethyl carbonium ion can be considered to be less stable than the triphenylmethyl ion derived from benzpinacolyl alcohol, the amount of cleavage is far less. In three runs at various temperatures, the amount of cleavage in the alcohol oxidized was 10.4, 16.3, and 25.5 per cent. In one run under reflux, the acetone resulting from cleavage was chlorinated (26). The products reported were pinacolone, acetone, acetaldehyde, and *t*-butyl alcohol. The chromyl chloride adduct was isolated from ligroin but not analyzed.

(*c*) *t-Butylphenylcarbinol:* Since the degree of hindering of this alcohol is intermediate between that of benzpinacolyl alcohol and pinacolyl alcohol, the cleavage was also intermediate in amount, being about 36 per cent. Products recovered were *t*-butyl phenyl ketone from normal oxidation and acetaldehyde from cleavage. Oxidations of this alcohol with chromic anhydride were also performed. Cleavage was less and was reduced to zero by manganous ion, whereas cleavage was unaffected by manganous or cerous ion in chromyl chloride oxidation (26). However, mercuric ion did reduce cleavage, perhaps by removal of the chloride.

(*d*) *t-Butyl-p-tolylcarbinol:* The cleavage reaction proceeds to the extent of 90 per cent (173).

(*e*) *p-Anisyl-t-butylcarbinol:* Here, also, about 90 per cent cleavage is observed (173).

7. Ketones and chlorinated ketones from saturated hydrocarbons

(*a*) *From 2-methylbutane:* A cooled solution of 2-methylbutane in carbon disulfide formed an addition compound containing two moles of chromyl chloride. At 110°C. this addition product evolved hydrogen chloride. After decomposition with water a chlorinated ketone was separated by means of sodium bisulfite. Analysis showed its composition to be C_5H_9OCl, which corresponds to 1-chloro-3-methyl-2-butanone. The chlorination probably took place at an early stage because the same chloroketone was obtained starting with 1-chloro-3-methylbutane (56). Unidentified aldehydes and acids also were noted. Hobbs and Houston (122) confirmed almost quantitative yields of the two-mole addition product; however, they reported on hydrolysis small amounts of the corresponding 3-chloro products. In either event the attachment of the chromyl chloride was to the No. 2 carbon atom. The decomposition of the addition product to form ketones was similar to the formation of acetophenone from ethylbenzene (reaction I).

(*b*) *From hexane:* Étard (56) carried out the chromyl chloride reaction with hexane in the same manner as with 2-methylbutane, obtaining a bisulfite product which yielded a chlorinated ketone analyzing $C_6H_{11}OCl$ and also appreciable amounts of a chlorohexane. Hobbs and Houston (122) obtained with hexane a 31.5 per cent yield of the chromyl chloride addition product; however, they reported that its analysis corresponded to approximately three moles of chromyl chloride per mole of hydrocarbon. Their products on hydrolysis were 2-hexanone, 3-hexanone, and high-boiling unsaturated ketones. These authors noted that the addition compound formed more slowly with hydrocarbons not possessing a methyl side chain.

(*c*) *From methylpentanes:* A nearly quantitative yield of the chromyl chloride addition product was obtained with 2-methylpentane. The molecular ratio was not determined. On hydrolysis a moderate yield of the two ketones, 4-methyl-3-pentanone and 4-methyl-2-pentanone, resulted (122).

3-Methylpentane gave a nearly quantitative yield of the chromyl chloride addition product with the normal two-mole composition. On hydrolysis there was a small yield of 3-methyl-2-pentanone (122).

(*d*) *From 2,2-dimethylbutane:* Although the adduct was not isolated or analyzed, a 9.5 per cent yield of pinacolone was obtained by the oxidation of 2,2-dimethylbutane with chromyl chloride in carbon tetrachloride (26). The reaction was allowed to proceed for one week before hydrolyzing the reaction mixture, and at the end of this time 82 per cent of the original hydrocarbon was unreacted. The pinacolone results from the normal Étard reaction (reaction I).

(*e*) *From 2,2-dimethylpentane:* On reacting chromyl chloride with 2,2-dimethylpentane for 90 days, a 19 per cent yield of a two-mole addition product resulted (122), which on hydrolysis formed unidentified oxygen-containing products, probably ketonic.

(*f*) *From 2,2,4-trimethylpentane:* With 2,2,4-trimethylpentane a nearly quantitative yield of a two-mole chromyl chloride addition product was obtained. On hydrolysis it gave a mixture containing relatively small amounts of an aldehyde, an acid, and a ketone, the formation of which was (122) explained as due to an intermediate carbonium ion. However, the formation of the aldehyde and acid appears to the authors to be similar to the normal Étard reaction (reaction I), with the attachment taking place at carbon atom 5, or to be a cleavage reaction due to attachment on both carbon atoms 4 and 5 (reaction IX).

(*g*) *From n-heptane:* The behavior of chromyl chloride with heptane appeared to be the same as with 2-methylbutane; however, additional work is needed, because isomers may have been present (56).

(*h*) *From 2,5-dimethylheptane:* A three-mole chromyl chloride addition product was reported with 2,5-dimethylheptane (122). The products of its hydrolysis were not identified.

(*i*) *From 2,7-dimethyloctane:* With 2,7-dimethyloctane a four-mole chromyl chloride addition product was reported (37). The products of hydrolysis were not determined. In general, mole ratios higher than two have been reported only for a few long-chain hydrocarbons. In no case have sufficient data been given to establish their molar ratios definitely.

(*j*) *From cyclohexane:* A two-mole addition product was formed by heating cyclohexane and chromyl chloride without a diluent for 2 days. On hydrolysis the chief product was cyclohexyl chloride obtained in 14 per cent yield (31). Traces of cyclohexanone also have been reported (122).

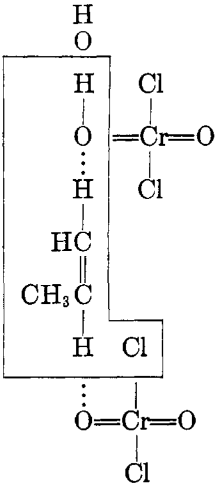
(*k*) *From methylcyclohexane:* A 25 per cent yield of hexahydrobenzaldehyde was obtained (246). Thus the behavior of chromyl chloride with a methyl-substituted cycloparaffin followed the normal pattern (reaction I).

(*l*) *From bicyclohexyl:* This substance formed an addition product with chromyl chloride (122). The products of its hydrolysis were not reported.

8. Chlorohydrins from olefins

(*a*) *From ethenes:* The behavior of chromyl chloride with ethylene itself has not been reported, nor has its behavior with mono- or dichloroethylenes. Tri- and tetrachloroethylenes did not form addition products with chromyl chloride (31), being miscible with it without reaction.

(*b*) *From propene:* A 43 per cent yield of propylene β-chlorohydrin was obtained by running propene gas into an ice-cooled, rapidly stirred solution of 155 g. of chromyl chloride in 300 ml. of carbon tetrachloride until the red color of chromyl chloride disappeared. The solution absorbed 0.55 mole of propene per mole of chromyl chloride. The chlorohydrin was obtained by decomposing the separated chromyl chloride addition product in the customary manner with a cold dilute solution of sodium bisulfite (31). Attachment of the chromyl chloride appeared to be to hydrogens on each side of the double bond (reaction XIII).



(XIII)

(*c*) *From butenes:* A 49 per cent yield of butylene β-chlorohydrin was obtained from 1-butene (reaction XIII). With 1-chloro-2-butene a one-mole chromyl chloride addition product resulted. As would be expected from the behavior of other compounds having a monochlorinated methyl group, it was not possible to introduce a second mole of chromyl chloride. The products of hydrolysis were not determined.

Only polymeric substances formed in the reaction of chromyl chloride with 2-methylpropene (31). The addition product shown for the propene (reaction XIII) would not form because hydrogens were not available on both sides of the double bond.

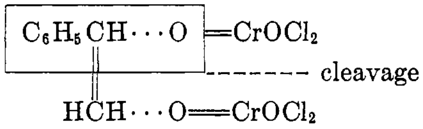
(*d*) *From 1-pentene:* A two-mole chromyl chloride addition product was obtained with 1-pentene. On hydrolysis there was a 43 per cent yield of amylene β-chlorohydrin (reaction XIII) (31).

(*e*) *From 1-hexene:* A 36 per cent yield of hexylene β-chlorohydrin was obtained from 1-hexene (31) (reaction XIII).

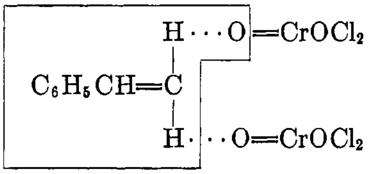
(*f*) *From cyclohexene:* A 52 per cent yield of *trans*-cyclohexene chlorohydrin was obtained (31) by adding dropwise a solution 310 g. of chromyl chloride in 150 ml. of carbon tetrachloride to a solution of 82 g. of cyclohexene in 200 ml. of carbon tetrachloride, using a 1-liter flask fitted with a dropping funnel, reflux condenser, and stirrer. Analysis of the brown precipitate corresponded to $C_6H_{10}(CrO_2Cl_2)_2$. This solid was decomposed by adding it portionwise to 400 ml. of ice water containing sodium bisulfite. After hydrolysis the organic layer was separated. The aqueous layer was extracted with ether and combined with the organic layer. After purification it yielded the above chlorohydrin. It is interesting to note that this addition yields the stereoisomer of that obtained with hypochlorous acid. Apparently, the chromyl chloride attached at both sides of the double bond. On hydrolysis, chlorination resulted in the elimination of the double bond (reaction XIII). Another batch prepared as above, but at a low temperature with half the quantity of chromyl chloride, yielded no water-soluble, organic product that was not volatile with steam, indicating that no diols were formed.

(*g*) *From 2,2,4-trimethyl-3-pentene:* With 2,2,4-trimethyl-3-pentene a two-mole chromyl chloride addition product also was obtained; however, the products of its hydrolysis were not identified (31). In the latter case, formation of a chlorohydrin is unlikely because this reaction could not occur without internal rearrangement.

(*h*) *From styrene:* A two-mole addition product was obtained by adding a 10 per cent solution of chromyl chloride in carbon disulfide to a cooled solution of styrene in the same solvent. It separated as a brown precipitate which, on washing with carbon disulfide and decomposing with water containing sulfurous acid, yielded a viscous brown liquid consisting chiefly of benzaldehyde together with traces of phenylacetaldehyde, benzoic acid, phenylacetic acid, and an unidentified chlorinated oil which was volatile with steam (111). The benzaldehyde probably resulted from attachment at both sides of the double bond followed by cleavage (reaction XIV). Phenylacetaldehyde could result from attachment on the methylene side of the double bond (reaction XV).



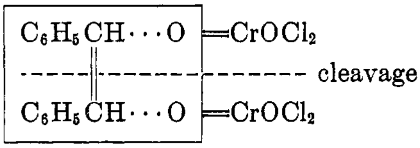
(XIV)



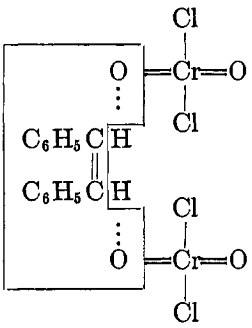
(XV)

(*i*) *From α-methylstyrene:* A solution of styrene in carbon tetrachloride, without cooling, yielded only polymeric substances with chromyl chloride. However, the α-methyl derivative, $C_6H_5C(CH_3){=}CH_2$, readily yielded a two-mole chromyl chloride addition product (31). Although the products of the hydrolysis of this addition compound were not determined, it is interesting that this reaction proceeded more smoothly with α-methylstyrene than it did with styrene itself.

(*j*) *From stilbene:* Although Cristol and Eilar (31) noted only polymeric substances from the reaction of chromyl chloride with stilbene, $C_6H_5CH{=}CHC_6H_5$, Henderson and Gray (111) reported a two-mole chromyl chloride addition product with stilbene, employing the same method as with styrene. On hydrolysis it decomposed to a brown oil and resinous matter, which after extraction with carbon disulfide, steam distillation, drying, and fractionation, yielded benzaldehyde and benzil together with a small amount of benzophenone and benzoic acid. There was no formation of diphenylacetaldehyde. Benzaldehyde resulted from cleavage (reaction XVI). Attachment on both sides of the double bond followed by oxidation could account for the diketone (reaction XVII). Benzophenone could result from the presence of a small amount of an asymmetric isomer such as 1,1-diphenylethylene. There is also the possibility of traces of 1,1-diphenylethane, which has close to the same boiling point.



(XVI)

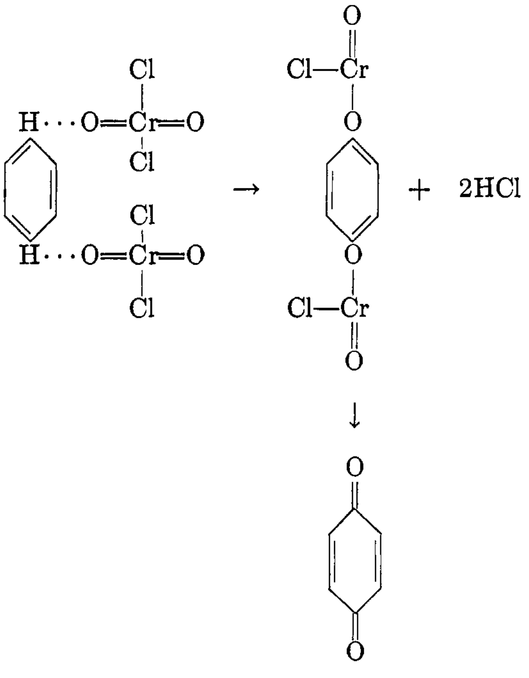


(XVII)

9. Formation of quinones

This oxidation involves hydrogens of two CH groups usually in the para position, whereas most Étard reactions are with hydrogens attached to the same carbon atom or to two adjoining carbon atoms. As in other Étard reactions, two formula weights of chromyl chloride are required for each one of the organic compound. Typical is the formation of quinone from benzene. No aldehyde or ketone formation has been established as occurring simultaneously with a quinone oxidation; however, chlorinated quinones are frequently encountered.

(*a*) *From benzene:* Étard carried out the formation of quinone by boiling an excess of benzene with chromyl chloride (four parts by weight of benzene to one of chromyl chloride) without a diluent. A brown precipitate separated with evolution of hydrogen chloride. Two moles of chromyl chloride combined with one of benzene. Two moles of hydrogen chloride were evolved, leaving a product having a composition corresponding to the formula $C_6H_4(CrO_2Cl)_2$. Decomposition of this addition product with water yielded chiefly quinone, presumably by rearrangement of the addition product during the evolution of hydrogen chloride (reaction XVIII). This quinone reaction was reported as specific for the para position; however, chlorinated orthoquinones may be possible. In the presence of glacial acetic acid, an almost quantitative yield of trichloroquinone was reported, together with traces of chloranil (23).



(XVIII)

(*b*) *From naphthalene:* With naphthalene Étard obtained a two-mole chromyl chloride addition product which on decomposition with water yielded a quinone analyzing as $C_{10}H_6O_2$ and presumably 1,4-naphthoquinone (reaction XVIII). In the presence of glacial acetic acid Carstanjen (24) obtained only resinous substances and chlorinated quinones such as dichloronaphthoquinone, $C_{10}H_4Cl_2O_2$.

(*c*) *From anthracene:* In the same general manner Étard obtained anthraquinones from anthracene. These anthraquinones were not identified; however, a tendency for them to retain chromium and chlorine was noted. Similar results were reported by others who employed special precautions to remove free chlorine from the chromyl chloride (98). Unidentified anthraquinones, both chlorinated and unchlorinated, also were obtained by treating chromyl chloride with anthracene in the presence of glacial acetic acid (24).

(*d*) *From phenanthrene:* This reaction was carried out in the same way. Phenanthrene combined readily with one mole of chromyl chloride at room temperature, and with two moles on heating (31). On hydrolysis a phenanthraquinone mixed with an unidentified resin was reported (111).

(*e*) *From halogenated benzenes:* Étard prepared bromoquinone and *p*-dibromoquinone, also chloroquinone and *p*-dichloroquinone, by the heated reaction of the corresponding halogenated benzenes with undiluted chromyl chloride, but did not give analyses of his products.

(*f*) *From nitrobenzene:* By refluxing on a water bath a 50 per cent solution of nitrobenzene in chloroform, to which was added slowly a solution of chromyl chloride, there resulted an evolution of hydrogen chloride and the precipitation of a dark brown powder. After it had been washed with chloroform and dried at 100°C., the compound gave analytical results corresponding approximately to the formula $NO_2C_6H_5(CrO_2Cl_2)_2$. When added to an excess of cold water the compound was decomposed with evolution of heat, and a clear heavy liquid separated consisting almost entirely of nitrobenzene. This behavior was analogous to the regeneration of *o*-nitrotoluene (reaction V). In treating nitrobenzene with chromyl chloride Étard obtained a product which he called *p*-nitroquinone because his analysis corresponded to that of this quinone; however, Henderson and Campbell (109) showed that it was *p*-nitrobenzoic acid resulting from traces of *p*-nitrotoluene in the nitrobenzene. Carstanjen (24) obtained trichloronitrobenzoic acid by treating nitrobenzene with chromyl chloride in the presence of glacial acetic acid.

(*g*) *From dinitrobenzenes:* As in the case of the nitrotoluenes no chromyl chloride addition product separated when more than one nitro group was present.

(*h*) *From phenol:* According to Étard chromyl chloride formed with phenol a brown addition product of indefinite composition which on decomposition with water yielded chiefly bis(hydroxyphenyl) ether. Trichloroquinone and chloranil were formed in the presence of glacial acetic acid (24). Details were not given regarding these reactions.

(*i*) *From cresols:* Chromyl chloride formed addition products of indefinite composition with *o*- and *p*-cresols. Decomposition by water in the presence of sulfur dioxide yielded alkali-soluble compounds which Étard called "quinones." The product formed from *o*-cresol analyzed as $C_7H_6O_3$; that from *p*-cresol as $C_{14}H_{10}O_3$. It is possible that the $C_7H_6O_3$ "quinone" was salicylic acid, resulting from the oxidation of the methyl group. However, this would be surprising, because the methyl group of a cresol is not oxidized to carboxyl by chromic acid. The $C_{14}H_{10}H_3$ "quinone" may have been benzoic anhydride produced via toluene.

(*j*) *From phenetole:* This ether, $C_6H_5OCH_2CH_3$, formed an addition product with chromyl chloride. On hydrolysis it gave an unidentified chlorinated compound which Étard called a "quinone." This work with phenetole, as well as that with the phenols, should be viewed as being of an exploratory character.

F. OTHER ORGANIC REACTIONS

By far the majority of the organic reactions of chromyl compounds can be classed as variants of the Étard reaction, which has already been discussed. Other organic reactions include miscellaneous oxidations, chromyl compounds as igniting agents, and the production of chromium complexes or chelates.

1. *Miscellaneous oxidations*

There is one early general discussion of this subject (75), and it was noted that chromyl compounds oxidized organic materials vigorously (147). One of the earliest reactions noted was that with carbon tetrachloride on heating (presumably to 400–500°C.); phosgene, chromic chloride, and chlorine were formed (49, 51, 52).

$$2CCl_4 + CrO_2Cl_2 \rightarrow 2COCl_2 + CrCl_3 + \tfrac{3}{2}Cl_2$$

Chromyl chloride has been suggested for the destruction of organic matter in toxicological analysis (183).

Chromyl fluoride is reported to be very active with organic materials (50, 248, 249). Ethanol and ether react to give chromic fluoride. Benzoic acid is reportedly converted to difluorobenzoic acid (131, 132), but this may be due to the presence of fluorine as an impurity; early preparations of chromyl fluoride sometimes contained free fluorine (50).

A wide variety of organic materials have been tested qualitatively for their behavior in chromyl chloride (43). The results are given in table 4.

Two groups of patents have been issued for processes depending on the oxidizing character of chromyl chloride. One (28, 46, 47, 238, 239) deals with the refining of hydrocarbon oils by reaction with chromyl chloride. The Étard reaction proceeds with certain constituents of the oil; the addition complex is hydrolyzed, and ketonic and aldehydic materials are separated. The residual oil is improved, particularly as regards its low-temperature properties.

A second group of patents (44, 45) covers the action of chromyl chloride on animal and vegetable oils. The oil is reportedly altered, particularly insofar as improved corrosion inhibition is provided. The altered oils are brown to green in color and presumably contain chromium(III) soaps.

2. *Chromyl compounds as igniting agents*

With a wide variety of organic materials, the oxidizing action of chromyl compounds is so vigorous that ignition takes place on mixing, since the heat of oxidation is not dissipated before the kindling temperature is reached. For this reason, care should be used in mixing chromyl compound with combustible or oxidizable compounds, for many of the ignition reactions proceed with almost explosive violence.

There is a wide variation in the ignition properties of chromyl compounds. Most vigorous is chromyl nitrate, which ignites benzene instantaneously (219), as well as saturated aliphatic hydrocarbons. The scattered data available on chromyl fluoride (50, 226, 248, 267) seem to place it in an intermediate position, less reactive than the nitrate but more reactive than the chloride. Other chromyl compounds are too unstable to have been evaluated.

The oxidizing activity of chromyl chloride may be increased by dissolving chromic acid therein.

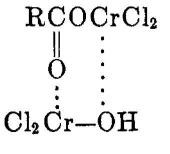
A partial list of compounds and materials ignited by chromyl chloride follows (43, 156, 241, 242, 243, 253, 254, 269): turpentine, methanol, ethanol, 2-propanol, 1-butanol, cyclohexanol, various commercial hydrocarbon fractions, α-pinene, ethyl ether, pyridine, *p*-cymene, ethylene glycol, 2-ethyl-1-hexanol, aniline, *t*-octylamine, *t*-butylamine, triethanolamine, cyclohexylamine, dicyclohexylamine.

Chromyl chloride does not ignite acetone, although this has been reported (156).

3. Production of chromium complexes

Descriptions of these reactions of chromyl compounds are found entirely in the patent literature. The complexes produced have important uses in chemical technology; chromium complexes of stearic and methylmethacrylic acids have found use in water-proofing compositions under the trade names of "Quilon" and "Volan," and chromium complexes of organic dyes form the important class of "premetallized" dyes now used in the processing of wool and synthetic fibers.

In a typical example of the chromium complexes of fatty acids, stearato chromic chloride is produced by the reaction of a solution of 1279 parts of stearic acid and 207.5 parts of ethanol in 11,200 parts of carbon tetrachloride with a solution containing 1400 parts of chromyl chloride in 4800 parts of carbon tetrachloride. The chromyl chloride is added under reflux during about 2 hr., and refluxing is contiued for another half hour. Hexavalent chromium is completely reduced by the addition of a solution of 20 parts of ethanol in 128 parts of carbon tetrachloride and refluxing continued for 2 hr., when the carbon tetrachloride is distilled off, leaving a green glassy solid. The chromium complex is purified by treatment to remove methanol-insoluble substances. The yield is 2800 parts (124). It is postulated that two chromium-chlorine residues are coördinated with each mole of stearic acid, the formula being of the following type:



$$\begin{array}{l} \mathrm{RCOCrCl_2} \\ \quad\ \| \qquad \vdots \\ \quad\ \mathrm{O} \qquad \vdots \\ \quad\ \vdots \qquad \vdots \\ \mathrm{Cl_2Cr{-}OH} \end{array}$$

There is no experimental evidence for these structures, which provide a coördination number of four for trivalent chromium. The additional two coördination positions may be filled by polymerization or by coördination with the alcoholic solvent in which these materials are usually supplied. In the above formula R is usually an alkyl group containing ten or more carbon atoms to produce the desired hydrophobic properties.

By a similar process, abietato chromic chloride is prepared using rosin as a starting material (125). The stearato compound may also be prepared continuously in 2-propanol solution (126). Chromium complexes of fluorinated acids such as *n*-enneafluorobutyric acid, $CF_3(CF_2)_3COOH$, *n*-undecafluorocaproic acid, $CF_3(CF_2)_4COOH$, and perfluorocyclohexanecarboxylic acid, $C_6F_{11}COOH$, are prepared by a process similar to that described above (162, 198). Ethanol is used as reducing agent. The fluoro derivatives are claimed to possess both water-repellent and oil-repellent properties.

Chromium complexes of mordant dyes soluble in organic solvents can be prepared by direct action of chromyl chloride on the organic dye (80). The acid properties of chromyl chloride serve to produce the desired derivative of the dye, while the action of the chromyl chloride also furnishes the chromium for complexing. Presumably a reducing agent is employed to prevent destruction of the dye molecule and produce chromium(III) for complexing. These reactions are thus similar to those employed for producing the fatty acid complexes described above.

The chromium–collagen complex characteristic of chrome-tanned leather can be formed directly on hides and furs by the action of chromyl chloride vapor after suitable preliminary treatment of the hides or furs (142).

4. Ester formation

The reaction of *t*-butyl alcohol with chromyl chloride at −50°C. gives red needles which are believed to be *t*-butyl chromate. They explode on warming above 0°C., and the reaction of the alcohol with chromyl chloride at higher temperatures proceeds explosively (26).

G. THERMOCHEMISTRY OF CHROMYL COMPOUNDS

The thermochemistry of chromyl compounds has been very little investigated, and the work is old. The heat of formation of chromyl chloride was estimated from the heat of hydrolysis (11, 12), which has been variously measured as 16.67 kcal./mole (13, 14) and 17.86 kcal./mole (170). From these data the heat of formation of the vapor at 18°C. has been postulated (130) as 122.67 kcal./mole and of the liquid as 131.15 kcal./mole. This gives a value for the latent heat of vaporization of 8.48 kcal., as compared with that given in Section II,C of 8.33 kcal.

H. PHYSIOLOGICAL EFFECTS OF CHROMYL COMPOUNDS

Little evaluation has been made of any action which is specifically attributable to chromyl compounds. When tested as a chemical warfare agent, chromic chloride was found to have three-tenths of the toxicity of chlorine (29). Étard (56) wrote: "After having used 5 kg, its management appears no more unpleasant or dangerous than that of bromine. Its irritant action has the special effect of producing hiccoughs." The authors may add that this "special effect" may have been a idiosyncrasy of Étard's, for no hiccoughs have been noted in their work with the compound.

Thomson (241, 242), who was rash enough to taste chromyl chloride, reported a "sweet, astringent, acid taste."

The fluoride is reported to produce "severe oppression of the lungs" (248, 249).

The ready hydrolysis of chromyl compounds in the vapor phase suggests that their physiological behavior will be that of a mixture of chromium(VI) oxide and the appropriate acid. The action of chromium(VI) oxide is well described in standard texts (99). Liquid chromyl chloride on the skin hydrolyzes slowly and its action appears similar to that of chromium(VI) oxide. Even chromyl nitrate is not as corrosive to skin as either nitric acid or dinitrogen pentoxide (43).

One use has developed from the toxicity of chromyl chloride. A patent (148) proposes its use for removing parasites and microörganisms from seeds by fumigating with a mixture of chromyl chloride and carbon tetrachloride vapor. The small amounts of chromium remaining on the seeds act as a stimulant to growth.

I. MISCELLANEOUS PROPERTIES OF CHROMYL COMPOUNDS

It has been proposed to treat wool, after scouring, with either chromyl chloride in carbon tetrachloride or chromyl chloride vapor (96a, 97) in order to reduce felting tendencies.

Cellulosic materials, such as newsprint, cloth, or regenerated cellulose, may be made water repellent by exposing them to 2 per cent chromyl chloride vapor for 5 sec. at room temperature and then heating for 2 min. at 110°C. (127).

V. Conclusion

Many of the properties of the less well known chromyl compounds must be inferred from the characteristics of the better known chromyl chloride. The physical properties of chromyl chloride are those of a typical nonmetallic halide; its inorganic reactions show in addition the powerful oxidant properties of chromium(VI). However, many reactions which thermodynamics would predict either do not occur or occur to a limited extent because of the insolubility of many inorganic compounds in chromyl chloride. Chromium(VI) oxide dissolves and its solutions are even more vigorous oxidants than is the pure chloride.

The typical organic reaction is the Étard reaction, in which aldehydes or ketones are prepared from hydrocarbons. In this review, an attempt has been made to show a tentative mechanism by which the various results observed can be explained. While alkyl-substituted aromatic hydrocarbons give rather good yields of aldehydes, aliphatic and cycloaliphatic compounds give complex mixtures of products in which halogenation as well as oxidation occurs. Further work has been suggested which may serve to clarify the Étard reaction.

There are many discrepancies and unexplored channels of research in the reactions of chromyl compounds with inorganic and organic substances. This review is intended to point them out to future workers in the field.

In attempting to bring order out of the confusion which exists because of the age of much of the recorded literature, the authors have drawn freely on unpublished work performed in their own laboratory, principally by Robert C. East, to whom grateful acknowledgment is made. Other workers who have contributed information are mentioned in the references.

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[3] Where references are to books or long articles relating to other subjects, a single page number is shown indicating where the details of interest start. However, most references relate chiefly to the subject being reviewed, and it is necessary to refer to them in their entirety, showing the first and last page numbers of the articles. In addition, there are references of a continuing character, such as Étard's contributions, which refer to or correct earlier contributions. While given different reference numbers, they should be read as a unit, because erroneous conclusions may be drawn if they are read only in part.

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