platinum or gold electrodes be substituted for the usual calomel half cells to avoid a dangerous source of contamination.

ST. PAUL, MINN. RECEIVED OCTOBER 19, 1934

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Reactions of Thionyl Chloride and of its Thermal Decomposition Products with Oxalates and Formates

BY WALTER C. SCHUMB AND CLEMENT H. HAMBLET

In the course of a study of the thermal decomposition of thionyl chloride, it was found necessary to determine the quantity of undecomposed thionyl chloride in the presence of its decomposition products, *viz.*, sulfur monochloride and dichloride, chlorine and sulfur dioxide.[1] Among the various reactants which were considered for this purpose, lead oxalate and lead formate were found to offer the most promise. Both react readily with thionyl chloride with the production of carbon monoxide, but since the exact nature of the reactions involved does not appear to have been established, it was considered of interest to investigate these reactions quantitatively, and to study also the reactions of the decomposition products of thionyl chloride with the same lead salts. As a result of this investigation, the nature of these reactions has been established, and, in addition, a method has been devised by which unchanged thionyl chloride may be determined in the presence of its decomposition products.

Preparation and Purification of Materials

Nitrogen.—Purified nitrogen was used in all of these experiments to sweep out the system and to carry along the vapors of volatile substances formed therein. Commercial nitrogen was purified by passage in succession through concentrated sulfuric acid, sodium hydroxide on asbestos ("Ascarite") and a tube 91 cm. long containing metallic copper (wire form, reduced from the oxide) at 550°. To eliminate hydrogen, which appeared to be evolved slowly by the reduced copper, the gas was passed over copper oxide at 550°, and the final drying of the gas was by means of anhydrous barium perchlorate ("Desicchlora") and phosphorus pentoxide (resublimed in oxygen).

Thionyl Chloride.—The thionyl chloride was obtained by purifying Eastman thionyl chloride (b. p. 76–78°) according to the method of Meyer and Turnau[2] in an all-glass apparatus, and was preserved in small, sealed capsules until ready for use.

As a criterion of the purity of this product, the heating curve of a portion was determined by means of an apparatus similar to that employed by Skau.[3] Since the flat portion of the curve, during which the temperature remained constant within five microvolts, lasted half the period during which actual melting was taking place, the thionyl chloride was considered to be of a high degree of purity. The melting point of thionyl chloride, as taken from the flattest part of this curve, was $-101.4°$, a value somewhat higher than the value ($-104.5°$) reported by Mayes and Partington.[4]

Sulfur Monochloride.—Sulfur monochloride (Merck) was purified by the method recommended by Pope, *et al.*[5] The all-glass apparatus was constructed so that the fractional distillations could be carried out, and the purified samples sealed off in small capsules, all in the absence of air.

"Sulfur Dichloride" Mixture.—Since sulfur dichloride is unstable at ordinary temperature, the pure substance could not be used; consequently a mixture of sulfur monochloride saturated at 0° with chlorine gas was employed. Commercial chlorine was dried by concentrated sulfuric acid, and then bubbled through 100 cc. of purified sulfur monochloride at 0°, at the rate of 1 cc. per second for forty-eight hours. At the end of this time, since the mixture showed no further deepening of color, the product was thoroughly frozen, and, after the system had been evacuated, distilled with the aid of liquid air into capsules, and sealed off.

Chlorine and Sulfur Dioxide.—These gases were dried by passage through concentrated sulfuric acid.

Lead Oxalate.—The lead oxalate used in the study of the individual reactions was a commercial product of good quality, and was not further purified. In the determination of the precision of the method of analysis for thionyl chloride in the presence of its decomposition products, the lead oxalate used was prepared metathetically from a slight excess of reagent quality oxalic acid and lead acetate. The product was washed with cold water and alcohol, and dried at 140°. Upon titration with potassium permanganate, the material was found to be 100.0% PbC_2O_4 on the basis of its reducing power.

Lead Formate.—The lead formate used was prepared by the action of a slight excess of formic acid on lead carbonate. The product was crystallized at 0°, washed with water, and dried at 110°. Titration of the crystals by the method of Blackadder[6] showed that on the basis of its

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[1] Heumann and Kochlin, *Ber.*, **16**, 1628 (1883).

[2] Meyer and Turnau, *Monatsh.*, **28**, 153 (1907).

[3] Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

[4] Mayes and Partington, *J. Chem. Soc.*, 2594 (1926).

[5] Pope, *et al.*, *ibid.*, **119**, 634 (1921).

[6] Treadwell–Hall, "Analytical Chemistry," 1930, p. 532.

reducing power the material contained 99.95% $Pb(OOCH)_2$.

Reactions with Lead Oxalate

A. The Reaction between Thionyl Chloride and Lead Oxalate.—Moureu[7] found that thionyl chloride reacted with the oxalates of sodium, lead, mercury and silver according to the general equation

$$M_2C_2O_4 + SOCl_2 \rightarrow SO_2 + 2MCl + CO_2 + CO$$

where M represents a monovalent metal. No indication as to how quantitatively this reaction with lead oxalate took place was given, other than the statement that sufficient heat was evolved by the reaction to raise the temperature of an excess of thionyl chloride to its boiling point.

In order, therefore, to determine the extent to which this reaction will proceed to completion when a known amount of thionyl chloride is passed over an excess of warm lead oxalate, the carbon monoxide evolved was determined gravimetrically, by first oxidizing it to carbon dioxide, and then absorbing this carbon dioxide in a weighed absorption tube containing sodium hydroxide on asbestos.

A weighed capsule, containing purified thionyl chloride, was introduced into the apparatus, from which the air was removed by a slow stream of purified nitrogen. After the capsule was broken, by means of a magnetic hammer, the thionyl chloride was allowed to volatilize at room temperature and to be swept along by the stream of nitrogen. The mixture passed successively through tubes containing lead oxalate heated to 60°, separated at intervals by plugs of glass wool; calcium chloride, to prevent back diffusion of moisture and the consequent hydrolysis of thionyl chloride; a 33% solution of potassium hydroxide to absorb acid gases, *i. e.*, carbon dioxide, sulfur dioxide and possibly thionyl chloride; sodium hydroxide on asbestos to remove last traces of acid gases and spray from the potassium hydroxide solution; cupric oxide wire, heated to 550°, to oxidize the carbon monoxide to carbon dioxide; and finally through an absorption tube (A) containing sodium hydroxide on asbestos, to absorb the carbon dioxide thus formed. A second similar absorption tube (B) followed by a guard tube, also containing sodium hydroxide on asbestos, acted as an over-all counterpoise, correction being made to the gain in weight of (A) according to the gain or loss in weight of (B). Since the rate of gas passage was slow ($^1/_3$ liter of nitrogen per hour) it was found necessary to use a third absorption tube (C) containing sodium hydroxide on asbestos *before* the cupric oxide tube to absorb carbon dioxide which diffused backward against the gas stream. The apparatus was constructed entirely of glass with the exception of the connectors to the absorption tubes, which were short lengths of pure gum rubber tubing.

In carrying out a run, nitrogen was first swept through the apparatus until the absorption tubes A, B and C remained constant to a milligram in weight during a 24-hour period. The sum of the gains in weight of the tubes A and B, each corrected by the change in weight of C, was taken as the weight of the carbon dioxide formed from the carbon monoxide. The weight of the thionyl chloride used was found by subtracting the weight of the glass fragments from the weight of the original filled capsule. The results of two runs are shown in Table I.

TABLE I

REACTION OF THIONYL CHLORIDE WITH LEAD OXALATE

Thionyl chloride taken		Lead oxalate	Carbon dioxide (formed from CO)		Percentage error
G.	Mole	taken, g.	G.	Mole	
1.4901	0.012524	55.8	0.5481	0.01246	−0.48
1.4918	.012538	50.0	.5490	.01248	− .48

These data indicate that the reaction

$$Pb(OOC)_2 + SOCl_2 \longrightarrow SO_2 + PbCl_2 + CO_2 + CO \quad (1)$$

at 60° proceeds quantitatively within the experimental error.

B. The Reaction between Sulfur Monochloride and Lead Oxalate.—Denham[8] studied the action of sulfur monochloride on the sodium and silver salts of monobasic organic acids in such solvents as light petroleum, ether and benzene. He was able to isolate, in certain cases, unstable intermediate products which decomposed on standing to the acid anhydride, sulfur dioxide and sulfur. The net reaction may be represented by the general equation

$$4RCO_2M + 2S_2Cl_2 \longrightarrow 4MCl + SO_2 + 3S + 2(RCO)_2O$$

He also investigated the action of sulfur monochloride on salts of dibasic acids such as oxalic, succinic and the three phthalic acids, and found that only the salts of succinic and phthalic acids appeared to react readily, and that they formed the corresponding anhydrides directly, *i. e.*, no intermediate compounds were isolated.

In the present work, preliminary experiments showed that sulfur monochloride reacts slowly with lead oxalate at room temperature with the formation of carbon monoxide, carbon dioxide, lead chloride, sulfur dioxide and free sulfur. To determine the molal proportions of these products, apparatus was employed, the operation of which depended as in the preceding case on the slow vaporizing of the liquid from a weighed capsule, broken in an atmosphere of nitrogen, through a tube containing lead oxalate. The lead oxalate was heated to 60° by means of an electric sleeve in order to cause the reaction to take place at an appreciable rate.

Unchanged sulfur monochloride was removed by passing the gas through a series of three horizontal tubes, containing mercury, agitated by an electrically driven shaker, and connected to the rest of the apparatus by glass spirals at both inlet and exit ends. A trap immersed in a carbon dioxide–alcohol bath followed the agitator to prevent back diffusion of moisture.

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[7] Moureu, *Compt. rend.*, **119**, 337 (1894).

[8] Denham, *J. Chem. Soc.*, **95**, 1235 (1909).

TABLE II

REACTION OF SULFUR MONOCHLORIDE WITH LEAD OXALATE

Lead oxalate, g.	Products (mole × 10^{-2})					Molal ratio (referred to $PbCl_2$)					S_2Cl_2 reacted, %
	CO	CO_2	SO_2	S	$PbCl_2$	CO	CO_2	SO_2	S	$PbCl_2$	
60	4.80	4.74	..	7.00	4.80	2.00	1.98	...	2.92	2.00	60[a]
49	4.45	4.41	2.10	6.50	4.40	2.02	2.00	0.955	2.96	2.00	49

[a] The coincidence that 60% of S_2Cl_2 reacted when 60 g. of lead oxalate was used has no significance; but the *proportionality* seen between the quantities in the *two* runs is clearly due to the fact that the percentage of S_2Cl_2 reacted depends upon the time of contact with the lead oxalate, and the more lead oxalate in the reaction tube, the longer the time of contact and hence the greater the amount of S_2Cl_2 entering into reaction.

Experiments also had shown that *sulfur dioxide* could be absorbed quantitatively from a gas stream by lead dioxide, provided that the latter were moist. To ensure the presence of sufficient moisture, the gas was bubbled through water before passage through the tube containing moistened lead dioxide. The effluent gas, being now saturated with moisture, was dried by calcium chloride and by resublimed phosphorus pentoxide before absorption of carbon dioxide and carbon monoxide.

The *carbon dioxide* was removed from the gas stream by an absorption tube containing sodium hydroxide on asbestos.[9] As in the previous case, *carbon monoxide* was oxidized to carbon dioxide by hot cupric oxide, and the carbon dioxide absorbed by a system of absorption tubes preceding and following the cupric oxide. The entire apparatus was also constructed entirely of glass with the exception of the connectors to the absorption tubes. The procedure employed in carrying out a run was much the same as that described in the preceding section.

At the end of a run the *sulfur dioxide* absorbed by the lead dioxide tube was determined by leaching the lead sulfate from excess lead dioxide by 3 *N* ammonium acetate solution, precipitating the lead by ammonium carbonate solution, and determining the sulfate in the filtrate as barium sulfate according to the method of Hintz and Weber.[10] Since the first precipitate invariably was contaminated by impurities, presumably acetate, it was fused with sodium carbonate before the final precipitation with barium chloride. Preliminary experiments with known amounts of sulfur dioxide showed that this analytical procedure gave results approximately 5% low.

The free *sulfur* deposited in the lead oxalate tube was extracted in a Soxhlet extractor with sulfur-free acetone, the solution transferred to a Carius tube, and the sulfur oxidized to sulfate, after evaporation to dryness, by concentrated nitric acid. After displacing the nitric acid by repeated evaporation with addition of hydrochloric acid, the sulfate was precipitated with barium chloride, filtered, ignited and weighed as barium sulfate.

The *lead chloride* formed in the lead oxalate tube was extracted with hot water in a Soxhlet apparatus, and the chloride precipitated with silver nitrate solution. The silver chloride precipitate was then dissolved in ammonium hydroxide, reprecipitated by addition of nitric acid and a small amount of silver nitrate solution, filtered, dried and weighed. The results of two runs are listed in Table II.

In view of the fact that, aside from the sulfur dioxide (which previous experiments had shown might be expected to be approximately 5% low), the number of moles of the various products bore a ratio to the lead chloride which varied from an integer by only about 1%, it is felt that a single reaction took place between the sulfur monochloride and the lead oxalate, and that this reaction could be represented by the equation

$$2S_2Cl_2 + 2Pb(OOC)_2 \longrightarrow 2CO + 2CO_2 + SO_2 + 3S + 2PbCl_2 \quad (2)$$

C. Reaction of Chlorine with Lead Oxalate.—Although it was reasonable to suppose that these substances should interact as follows

$$Cl_2 + Pb(OOC)_2 \longrightarrow PbCl_2 + 2CO_2 \quad (3)$$

it seemed advisable to verify this assumption experimentally, in view of the fact that no discussion of this reaction could be found.

In an all-glass apparatus dry chlorine gas, contained in a flask, was swept by means of a slow stream of purified nitrogen through a tube of warm lead oxalate. Unchanged chlorine was then removed from the gas mixture by passage through a mercury agitator, and the carbon dioxide and carbon monoxide in the residual gas were determined as before. The lead chloride formed was extracted from the lead oxalate by hot water, and the chloride in the extract determined as described in the preceding section. In this way the molal ratio of CO_2:$PbCl_2$ in the reaction products was found to be slightly under 2.00, the deviation being attributed to traces of hydrogen chloride,[11] which is invariably present in chlorine unless the latter be prepared under very special conditions. It is to be concluded, therefore, that the reaction of chlorine and lead oxalate at 85° proceeds as indicated in equation (3).

D. Reaction of Sulfur Dichloride with Lead Oxalate.—Since sulfur dichloride is an unstable substance obtainable at ordinary temperatures only in the presence of its decomposition products,

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(9) Due to the intensive drying of the gas passing through the phosphorus pentoxide tube, the absorption tube immediately following it decreased at a constant rate (0.0002 g. per liter of nitrogen passed), as determined in blank runs. Consequently, to determine the weight of the carbon dioxide absorbed, the total volume of nitrogen used was measured and a corresponding correction, amounting to approximately 5% of the total gain in weight, was made to the actual gain in weight.

(10) Hintz and Weber, *Z. anal. Chem.*, **45**, 31 (1906).

(11) Hydrogen chloride when passed over lead oxalate at 85° was found to be converted practically completely into lead chloride, and long needles of oxalic acid sublimed from the reaction tube. Evidently the reaction here is $2HCl + Pb(OOC)_2 \longrightarrow H_2(OOC)_2 + PbCl_2$.

chlorine and sulfur monochloride,[12] it seemed questionable whether the reaction of sulfur dichloride and lead oxalate would resolve itself into the two reactions (2) and (3) discussed in preceding sections, or whether the equation

$$4Pb(OOC)_2 + 3SCl_2 \longrightarrow 3PbCl_2 + PbSO_4 + 2S + 4CO + 4CO_2 \quad (4)$$

analogous to the equations proposed by Heintz[13] and by Carius[14] for the reaction of SCl_2 with salts of monobasic organic acids, would represent the facts. In any event, to test the validity of equation (4), derived from Heintz's results, account must be taken of reactions (2) and (3) which take place simultaneously.

The experimental method employed in the study of this reaction was essentially that used in the case of sulfur monochloride, described in section B. 1.65 g. of the dichloride mixture was allowed to act upon 44 g. of lead oxalate at 60°. All of the dichloride did not enter into reaction, as indicated by the attack of the mercury in the agitator. The products obtained, in millimoles, are

CO	CO_2	S	SO_2	$PbCl_2$
8.16	8.95	0.661	3.75	8.40

If the net reaction which took place were the sum of the reactions of chlorine and of sulfur monochloride with lead oxalate, the sum of the millimoles of CO and CO_2 produced should be twice the number of millimoles of lead chloride formed. This is not the case, since $(8.16 + 8.95)/2 = 8.55 \not\doteq 8.40$. A satisfactory check upon the validity of equation (4), as modified by reactions (2) and (3) operating simultaneously, is found in the calculation of the number of millimoles of $PbCl_2$ that should have been formed on this basis.

(3.75)(2) = 7.50 millimole
CO from (2) $\Bumpeq$ 7.50 millimoles $PbCl_2$
8.16 − 7.50 = 0.66 millimole
CO from (4) $\Bumpeq$ 3/4(0.66) = 0.495 millimole $PbCl_2$
8.95 − 8.16 = 0.79 millimole
CO_2 from (3) $\Bumpeq$ 1/2(0.79) = 0.395 millimole $PbCl_2$
Calculated 8.39 millimoles $PbCl_2$
Found 8.40

Equation (4), therefore, may be considered to be quantitatively in agreement with the data.

E. Sulfur Dioxide and Lead Oxalate.—It was demonstrated that when dry sulfur dioxide gas was swept by purified nitrogen through a tube packed with lead oxalate at 60°, no carbon monoxide was detectable in the issuing gas mixture, as indicated by the fact that, after removal of acid gases and passage of the gas through a tube of iodine pentoxide at 160°, thence into starch solution, no coloration was produced. Hence, sulfur dioxide is without action upon lead oxalate under these conditions.

Reactions with Lead Formate

F. The Reaction between Thionyl Chloride and Lead Formate.—Qualitative tests showed that the products formed when these substances reacted included lead chloride, carbon monoxide, sulfur dioxide and formic acid. Hence, by analogy with the reaction between thionyl chloride and lead oxalate, the following reaction might be expected to take place

$$SOCl_2 + Pb(OOCH)_2 \longrightarrow PbCl_2 + SO_2 + CO + HCOOH$$

In order to test this hypothesis, quantitative measurement of the various products was made. The apparatus used was similar to that described in Section A. Instead of a single absorbing solution of potassium hydroxide, however, there was used a series of three bubble tubes, each of approximately 10-cc. capacity, containing a solution of potassium hydroxide. The contents of these bubble tubes were washed out at the end of the run and aliquot parts analyzed for sulfite and formate content. The carbon monoxide produced was determined as before.

The sulfite in the solution of potassium hydroxide was determined as barium sulfate after oxidation by hydrogen peroxide in alkaline solution. The formate was determined volumetrically by the method of Blackadder,[6] after removal of sulfite from the solution by precipitation with barium chloride.

The results of one run, the lead formate being heated to 60° during the reaction, are as follows

Reactants: Thionyl chloride: 3.7260 g. $\Bumpeq$ 0.03130 mole; lead formate: 98 g.

Products		Molal ratio to thionyl chloride
Carbon monoxide (as CO_2): 1.2349 g. $\Bumpeq$	0.0281 mole	0.898
Sulfur dioxide:	0.03135 mole	1.00
Formic acid:	0.0344 mole	1.10

The absence of all but a negligible quantity of chloride in the absorbing solution of potassium hydroxide after the run indicated that all the chlorine in the thionyl chloride was converted to lead chloride.

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[12] Compare Lowry and Jessop, *J. Chem. Soc.*, 1421 (1929).

[13] Heintz, *Jahresber.*, **9**, 296 (1856); *Ann. der Physik*, **98**, 458 (1856).

[14] Carius, *Ann.*, **106**, 291 (1858).

It is seen that the molal ratios obtained are nearly, but not quite, in accord with the postulated equation. Although the sulfur dioxide is in quantitative agreement, the formic acid produced is 10% higher, the carbon monoxide a corresponding amount lower, than would be expected. The significance of these results is discussed below. Since the change in crystalline form of the material in the tube originally containing lead formate appeared complete and extended only a short distance from the end of the tube at which the thionyl chloride entered, the primary reaction appeared to have gone to completion.

G. The Reaction between Sulfur Monochloride and Lead Formate.—Qualitative tests showed that these substances reacted to form lead chloride, sulfur, sulfur dioxide, formic acid and carbon monoxide. The products were quantitatively studied, as in Part B, except that the sulfur dioxide and formic acid were absorbed in a 33% solution of potassium hydroxide which was divided into aliquot parts at the end of the run and analyzed for sulfite and formate content as in Part F.

The products determined in a single run were as follows, the lead formate being at room temperature during the reaction

Reactants: Sulfur monochloride: 2.4175 g. ≎ 0.0179 mole; lead formate: 90 g.

Products: Carbon monoxide: 0.6865 g. ≎ 0.0156 mole; sulfur dioxide: 0.00497 mole; formic acid: 0.0278 mole.

It was demonstrated, in the manner described in Section F, that all the chlorine in the sulfur monochloride that had entered into reaction was converted into lead chloride, and that the primary reaction had proceeded to completion.

In the data just given no simple relationship appears to exist between the products of this reaction. Suspecting that this might be due to a secondary reaction between sulfur monochloride and formic acid, these two substances were allowed to mix at 100° and the gaseous mixture then analyzed for sulfur dioxide and carbon monoxide. No appreciable quantities of these latter substances were detected. Hence, the failure of the proportions of the products of the reaction between sulfur monochloride and lead formate to conform to simple molal ratios could not be ascribed to this cause.

Although no conclusions can be drawn directly from the experimental data obtained from the reaction of sulfur monochloride on lead formate, analogy with the reactions discovered by Denham[8] would suggest the possibility of the intermediate formation of formyl sulfurous acid, $OS(OCHO)_2$, the acetyl derivative of which was prepared by Tommasi.[15] If 90% of the formyl sulfurous acid so formed decomposed spontaneously, as would be expected

$$OS(OCHO)_2 \longrightarrow SO_2 + CO + HCOOH$$

while the remaining 10% reacted with the alkali according to the equation

$$OS(OCHO)_2 + 4KOH \longrightarrow K_2SO_3 + 2HCOOK + 2H_2O$$

the total moles of formate would be 10% greater than the number of moles of thionyl chloride used, the moles of carbon monoxide produced would be less by the same amount, and the moles of sulfur dioxide would be the same as the number of moles of thionyl chloride—a condition which would be in accord with the data recorded above for this reaction.

H. Sulfur Dioxide and Lead Formate.—The possibility of reaction between these substances was investigated in a manner similar to that employed in Part E. No coloration of the starch occurred as the sulfur dioxide was allowed to pass over lead formate, indicating that no trace of carbon monoxide was evolved.

I. Determination of Thionyl Chloride in the Presence of its Decomposition Products.—Assuming the thermal decomposition of thionyl chloride to take place according to the equation

$$4SOCl_2 \longrightarrow S_2Cl_2 + 2SO_2 + 3Cl_2$$

followed by

$$S_2Cl_2 + Cl_2 \rightleftarrows 2SCl_2{}^{16}$$

it has been shown that the primary reactions of thionyl chloride and of its decomposition products with lead oxalate can be represented by equations (1), (2), (3), (4), with no reaction taking place with sulfur dioxide. Of these reactions, (1) is the only one which has been found to take place quantitatively under the conditions obtained. Moreover, the secondary reaction $Cl_2 + 2S \longrightarrow S_2Cl_2$ further complicates the application of lead oxalate directly to the analysis.

It was found possible, however, to simplify the mixture resulting from the pyrolysis of thionyl chloride by the expedient of reducing both sulfur dichloride and chlorine to sulfur monochloride.

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(15) Tommasi, *Ber.*, **7**, 826 (1874).

(16) This was concluded from the color change undergone by a sample of thionyl chloride when thermally decomposed, and is in accord with the observations of Lowry and Jessop (Ref. 12) on the sulfur–chlorine system.

Since elementary sulfur reacts vigorously with chlorine, and since sulfur dichloride is appreciably dissociated into sulfur monochloride and chlorine at ordinary temperatures, it appeared reasonable to expect that treatment of the mixture with an excess of sulfur would eliminate both of these compounds from the mixture to be analyzed. Furthermore, since Prinz[17] found it necessary to heat thionyl chloride to 180° with elementary sulfur before reaction occurred between these substances, it should be possible to carry out such a removal of chlorine and sulfur dichloride without loss of thionyl chloride.

The completeness of this reaction was determined colorimetrically since sulfur dichloride is the only deep-colored component of the mixture. Samples of the red dichloride mixture were heated in sealed tubes with an excess of precipitated sulfur until the color matched that of a sample of sulfur monochloride. No appreciable change occurred over an extended period at room temperature, but at 100° it was found that in one hour complete conversion of the red to yellow sulfur chloride took place.

Since the components in the mixture produced by the thermal decomposition of thionyl chloride could be reduced by this method to three—thionyl chloride, sulfur monochloride and sulfur dioxide—and since sulfur dioxide had been found not to react with lead oxalate, the problem of determining the amount of unchanged thionyl chloride in such a mixture was considerably simplified; for, by allowing such a mixture to react with lead oxalate after reduction of sulfur dichloride and chlorine, the thionyl chloride present could be calculated from a knowledge of the quantity of two different products formed by this reaction. Thus, if the sulfur liberated and carbon monoxide evolved were determined, the number of moles of thionyl chloride present would be: (moles of carbon monoxide) $-$ $^2/_3$ (moles of sulfur).

Determination of Free Sulfur.—Since the previously mentioned method of determining free sulfur deposited in lead oxalate did not give sufficiently accurate results, a method depending on the volatilization of the sulfur in the form of its chlorides and the subsequent oxidation of these chlorides to sulfate by means of concentrated nitric acid was tried and found to give greater precision. In a typical determination of sulfur, approximately 25 cc. of liquid chlorine was allowed to evaporate slowly and, after drying with calcium chloride, was allowed to pass through the tube containing the mixture of sulfur and lead oxalate, which was heated to 70–80°. The sulfur chlorides thus formed were swept along by the stream of excess chlorine and then were absorbed by concentrated nitric acid, passing in succession through three towers packed with glass beads, and constructed in such a way that the chlorine was forced to bubble through most of the nitric acid present (approximately 25 cc. in each tower). After all of the chlorine had been swept through, the contents of the absorption towers were repeatedly evaporated to dryness with hydrochloric acid, and the sulfate content of the residue determined as barium sulfate.

For the purpose of demonstrating the precision of this method, the carbon monoxide evolved when sulfur monochloride was allowed to act on lead oxalate was determined as described in Section B, and the sulfur simultaneously liberated was determined by the method given in the preceding paragraph. The results of two such determinations are as follows:

Millimoles of CO evolved	14.61	12.82
Millimoles of S calcd. from CO evolved	21.91	19.23
Millimoles of S found	21.79	19.30
Error, %	0.5	0.4

Precision of Determination of Thionyl Chloride in the Presence of its Decomposition Products.—An over-all check on the precision with which thionyl chloride may be determined in the presence of its decomposition products was made by mixing known quantities of sulfur monochloride and thionyl chloride, in the absence of moisture, and then determining the amount of thionyl chloride that could be accounted for by the proposed method.

Separate weighed capsules of thionyl chloride and of sulfur monochloride were broken *in vacuo* by magnetically-operated hammers, their contents distilled and condensed by means of liquid air in a tube, A (Fig. 1), containing an excess of free sulfur. The quantities of each of these materials were obtained, as before, by subtracting the weight of the capsule fragments from the weight of the original filled capsules. The tube A, containing the condensate, was heated as described above, and then broken *in vacuo* by a magnetically-operated hammer (the tube leading to the vacuum pump previously having been sealed off at H), the contents distilled from the excess of

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(17) Prinz, *Ann.*, **223**, 355 (1884).

sulfur and condensed, with the aid of liquid air, in a second tube, C, which was then sealed off at K. After opening valves B and D, the contents of C were swept by nitrogen through lead oxalate, and the carbon monoxide and sulfur produced by the resulting reaction determined as previously described. The results of two runs are shown in the table.

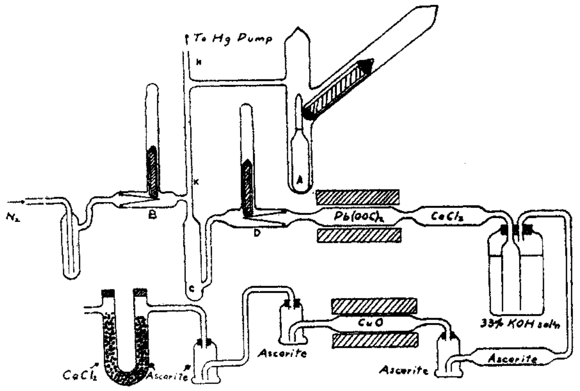

Fig. 1.

EXPERIMENTAL DATA

	$SOCl_2$ taken	S_2Cl_2 taken	CO_2 from CO	$BaSO_4$ from S	$SOCl_2$ calcd.	Error, %
G.	2.4177	2.0329	1.3990	4.0369	2.412	0.2
Mole	0.02032		0.03180	0.01730	0.02027	
G.	2.7315	2.8066	1.5541	4.3370	2.729	0.1
Mole	0.02295		0.03532	0.01858	0.02293	

The fact that the over-all error is smaller than the error involved in the individual determination of either carbon monoxide (Section A) or sulfur (Section I) is largely due to the fact that the error in both of these latter determinations tended to be negative, so that when combined, partial cancellation took place.

Summary

1. From the heating curve of purified thionyl chloride a new value for the melting point of this compound, −101.4°, has been determined.

2. The reactions of thionyl chloride and of its thermal decomposition products, sulfur monochloride and dichloride, and chlorine, with lead oxalate have been quantitatively investigated at 60°, and the equations involved in the last three reactions have been determined.

3. The reactions of thionyl chloride and of sulfur monochloride with lead formate have been investigated quantitatively. Although no simple reaction was found to take place in these cases, mechanisms based on the known behavior of substances in analogous reactions have been suggested to account for the results.

4. Sulfur dioxide has been found to react with neither lead oxalate nor lead formate at 60°.

5. Based on the reactions with lead oxalate and the quantitative reduction of chlorine and sulfur dichloride to sulfur monochloride by means of elementary sulfur, a method has been developed for the determination of thionyl chloride in the presence of its thermal decomposition products with a precision of 0.2%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. LOUIS UNIVERSITY]

The Parachor and Structure of Nickel Carbonyl

BY F. W. LAIRD AND M. ALONZA SMITH, S.L.

The present determination of the surface tension of nickel carbonyl has been undertaken in order to compute its parachor and to secure thereby evidence as to its structure. Since previous determinations of its surface tension were made in the presence of its decomposition products,[1] we have been particularly careful to make our measurements upon specially purified material.

Thiophene-free benzene was repeatedly dried over calcium chloride and distilled from phosphorus pentoxide, the main fraction coming over at 79.9° (corr.). The water was redistilled from alkaline permanganate. The nickel carbonyl, prepared by one of us,[2] was redistilled in a vacuum in a cold room at −2°.[3]

The surface tension was measured by the two-capillary method of Sugden.[4] In preliminary standardizing measurements the surface tension of water was measured at 10, 15 and 20° and values of 74.26, 73.54 and 72.71 were obtained, as compared with the values of Young and Harkins[5] of 74.22, 73.49 and 72.75, respectively. Simi-

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[1] Ramsay and Shields, *J. Chem. Soc.*, **63**, 1089 (1893).

[2] F. W. Laird, *Rec. trav. chim.*, **46**, 177–180 (1927).

[3] Initial attempts at drying over phosphorus pentoxide gave spontaneous ignition.

[4] Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, 1930.

[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. IV, p. 447.