[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

The Donor Properties of POCl₃, SeOCl₂, CH₃COCl, SOCl₂ and VOCl₃

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Freezing point diagrams are reported for the systems $POCl_3$–CCl_4, $POCl_3$–$SiCl_4$, $POCl_3$–$AsCl_3$, $SeOCl_2$–CCl_4, $SeOCl_2$–$AsCl_3$, $SeOCl_2$–$SnCl_4$, CH_3COCl–$SiCl_4$, CH_3COCl–CCl_4, CH_3COCl–$AsCl_3$, CH_3COCl–$SnCl_4$, CH_3COCl–$TiCl_4$, $SOCl_2$–CCl_4, $SOCl_2$–$SiCl_4$, $SOCl_2$–$AsCl_3$, $SOCl_2$–$SnCl_4$, $SOCl_2$–$TiCl_4$, $SOCl_2$–C_5H_5N, $VOCl_3$–$SnCl_4$ and $VOCl_3$–$TiCl_4$. Compounds observed indicate decreasing donor strength in the order $POCl_3$, $SeOCl_2$, CH_3COCl, $SOCl_2$, $VOCl_3$, and decreasing acceptor strength in the order $TiCl_4$, $SnCl_4$, $AsCl_3$, $SiCl_4$, CCl_4. Infrared spectral studies of the oxychloride-acceptor systems are reported.

Introduction

Metal halides exhibiting considerable variation in Lewis acid strength have been shown to form addition compounds with a variety of oxychlorides. In addition to POCl₃ compounds,[1] metal halide addition compounds with SeOCl₂,[2] CH₃COCl[3-7] and SOCl₂[8] have been reported. Most such compounds appear to be by-products of studies of the oxyhalides as aprotic solvent systems. Consequently no systematic study has been made of the extent to which oxyhalides form compounds with the normal halides. We have attempted such a study and report it herewith.

It is presumed that the oxychlorides behave as donors, and the series POCl₃, SeOCl₂, CH₃COCl, SOCl₂ and VOCl₃ was chosen as representative of wide variation in donor strength. The series CCl₄, SiCl₄, AsCl₃, SnCl₄ and TiCl₄ was chosen as representative of chlorides differing in acceptor strength. The freezing point diagrams of the several binary donor–acceptor systems were obtained. Three of the diagrams have been reported previously, POCl₃–TiCl₄,[9] POCl₃–SnCl₄[10] and CH₃-COCl–TiCl₄.[6] Two others, those of SiCl₄–SeOCl₂ and TiCl₄–SeOCl₂, were not obtained for reasons that will be made known. In light of the results obtained in the systems VOCl₃–TiCl₄ and VOCl₃–SnCl₄, no other VOCl₃ systems were measured. The SOCl₂–pyridine system was studied to estimate the extent to which the oxychlorides are capable of functioning as acceptors.

The structures of most of the addition compounds have yet to be settled, although NOCl·AlCl₃ has been shown to exhibit Raman spectra characteristic of NO⁺ and AlCl₄⁻,[11] and very recently the crystal structure of POCl₃·SbCl₅ was reported.[12] The infrared spectra of some of the oxychloride addition compounds and of the oxychlorides dissolved in excess TiCl₄, SnCl₄ and CS₂ have been investigated in an effort to elucidate the kind and degree of interaction present in the liquid state.

(1) V. Gutmann, *Z. anorg. allgem. Chem.*, **269**, 279 (1952).

(2) R. Weber, *Pogg. Ann.*, **125**, 135 (1865).

(3) A. Bertrand, *Bull. soc. chim. France*, **33**, 403 (1880).

(4) H. Meerwein and H. Maier–Huser, *J. prakt. Chem.*, **134**, 51 (1932).

(5) H. C. Brown, *et al.*, THIS JOURNAL, **61**, 678 (1939).

(6) N. M. Cullinane, *et al.*, *J. Chem. Soc.*, 4106 (1952).

(7) N. N. Greenwood and K. Wade, *ibid.*, 1527 (1956).

(8) H. Hecht, *Z. anorg. Chem.*, **254**, 37 (1947).

(9) W. L. Groeneveld, *et al.*, *Rec. trav. chim.*, **72**, 950 (1953).

(10) J. C. Sheldon and S. Y. Tyree, Jr., THIS JOURNAL, **80**, 4775 (1958).

(11) H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **72**, 21 (1953).

(12) I. Lindquist and C. I. Branden, *Acta Chem. Scand.*, **12**, 134 (1958).

Experimental

Reagents.—All reagents used were available commercially or from graduate student preparations except SeOCl₂ and VOCl₃. Each reagent was purified by distillation until boiling point agreed with literature values.

In most cases our freezing points agreed with the quoted values, e.g., POCl₃, 1.0° vs. 1.25°; SeOCl₂, 11.5° vs. 10.9°; SnCl₄, −32° vs. −33°; AsCl₃, −17° vs. −18°. However two exceptions are worthy of note. Our value for TiCl₄ and SOCl₂ were −24° and −101°, respectively, in comparison with the accepted values[13] of −30° and −105°. While we were engaged in the experiments, a new value of −24.115° was accepted for TiCl₄.[14] We have no explanation for the disparity between the values for SOCl₂. All handling and transferring of components were carried out in a dry box.[15]

Selenium(IV) Oxychloride.—The compound was prepared by the method of Smith and Jackson.[16]

Vanadium Oxytrichloride.[17]—AlCl₃ and V₂O₅ were mixed intimately and placed in a distillation apparatus. Upon very slow warming to a maximum of 400°, a yellow-orange distillate was obtained which is impure VOCl₃. Several redistillations were necessary to give the pure lemon-yellow liquid. *Anal.* Calcd. for VOCl₃: V, 29.4; Cl, 61.4. Found: V, 29.4; Cl, 60.7. Reported[18] b.p. 127°; f.p. −79.5°. Found: b.p. 126–129°; f.p. −79°.

Freezing Point Diagrams.—The cell was equipped with an efficient magnetic stirrer and a deep thermocouple well, reaching into the sample. Total sample weights varied from 20 to 50 grams. A five junction copper–constantan thermocouple was used as the temperature sensing device. The largest mv. reading (liquid N₂ point) was −5.45 mv. All readings were made to the nearest hundreth of a millivolt. The thermocouple was checked using the ice, carbon dioxide and liquid nitrogen points. Convection currents around the thermocouple were avoided by adding a low freezing liquid to the well in sufficient quantity to cover the junctions. Freezing points were recorded as the temperatures at which the last bit of solid disappeared during a period of slow warming. This technique was used to avoid supercooling, which proved to be very common in the systems studied. The error is believed to lie predominantly in judging the time at which the last crystals disappeared. We believe the error to be no greater than 1° down to 80°, and a maximum of 2° at −120°. Eutectic temperatures recorded on the diagrams for non-eutectic compositions were observed as temperature arrests during the periods of slow warming. Compositions were determined by weighing the cell after each addition. In some cases, the results represent one run per point, e.g., the CCl₄–POCl₃ system. In other cases, the results represent four or five runs over the entire composition range, e.g., the SnCl₄–SeOCl₂ system.

Selenium(IV)Oxychloride–Silicon Tetrachloride System.—The addition of small amounts of SeOCl₂ to SiCl₄ gave a thick pasty solid and a large heat evolution. The solid melted at no reasonable temperature, namely, in the vicinity of 300°. It was found that the same solid is formed upon mixing the two components in any ratio. The white solid

(13) "Handbook of Chemistry and Physics," 37th Ed., Chemical Rubber Publishing Co., Sandusky, Ohio, 1955.

(14) F. D. Rossini, *et al.*, "Properties of Titanium Compounds and Related Substances," ONR Report, ACR-17, 1956, p. 24.

(15) S. Y. Tyree, Jr., *J. Chem. Educ.*, **31**, 603 (1954).

(16) G. B. L. Smith and J. Jackson, *Inorg. Syntheses*, III, 130 (1950).

(17) We are indebted to Mr. J. Brown Goehring, of this department, for one sample of VOCl₃.

(18) F. R. Brown and D. A. Griffitts, *Inorg. Syntheses*, IV, 80 (1953).

sublimed to a brown vapor and recondensed to give a slightly yellow solid. A white crystalline precipitate formed slowly at room temperature upon mixing CCl_4 solutions of $SiCl_4$ and $SeOCl_2$. The white crystalline precipitate appeared to be identical with the white solid obtained upon mixing the two components in the absence of a solvent. Analyses of the white crystals show: Se, 36.5; Cl, 63.7; $SeCl_4$ requires: Se, 35.8; Cl, 64.2. We believe that $SiCl_4$ and $SeOCl_2$ react to give $SeCl_4$, despite the statement of Smith[19] that a $SiCl_4 \cdot 2SeOCl_2$ compound exists. It is significant that the article by Smith is a review article and no reference is given to the source of the information. A thorough search discloses no other reference to the compound.

Selenium(IV) Oxychloride–Titanium Tetrachloride System.—Mixing of the pure components at room temperature and in appropriate proportions does not give the yellow compound reported by Weber[2] or the white compound reported by Wise[20] in even reasonably pure condition. An exothermic reaction takes place. The product contains some TiO_2, as indicated by high Ti and low Cl analyses. Further, the infrared spectrum shows the broad band from 800 to 650 cm.$^{-1}$, with a maximum at 710 cm.$^{-1}$, characteristic of TiO_2. We believe that a reaction similar to that in the $SiCl_4$–$SeOCl_2$ system takes place.

A sample of the addition compound was prepared by mixing CCl_4 solutions of the two components. The crystals were sublimed at 120°, 5 mm., giving yellow prisms (*cf.* ref. 2).

Anal. Calcd. for $TiCl_4 \cdot 2SeOCl_2$: Ti, 9.15; Cl, 54.5; Se, 30.3. Found: Ti, 9.19; Cl, 53.6; Se, 30.2.

The compound decomposes upon heating much above 100° at atmospheric pressure. Upon repeated sublimation, a product is obtained which resembles $SeCl_4$. Analysis of such a product showed: Ti, 1.1; Cl, 62.6; Se, 36.0. Calcd. for $SeCl_4$: Cl, 64.2; Se, 35.8.

Infrared Spectra.—The spectra of solids were obtained in paraffin oil mulls; those of solutions were obtained in a special liquid cell, constructed in the departmental shop, employing polyethylene spacers for rapid diassembly. The cell was loaded in the dry box.[15]

Results and Discussion

Freezing Point Diagrams.—The results of the freezing point determinations are shown in Figs. 1–11, confirming the existence of $TiCl_4 \cdot CH_3COCl$[6] and $SnCl_4 \cdot 2SeOCl_2$[2] and indicating compound formation in several other cases. The over-all implications are summarized in Table I. Two of the compounds formed among the systems studied can be sublimed without appreciable decomposition. Such compounds are indicated in the table as "strong cpd." The majority of the compounds melt near or below room temperature, and it is possible to distil the components apart indicating much less interaction in the liquid state. Such compounds are termed "weak cpd." in the table. Some variation is to be observed within each category, however. Thus, $SeOCl_2$ and $SnCl_4$ can be distilled apart, whereas it is not possible to separate $POCl_3$ and $SnCl_4$ by distillation, the fractions boiling around 116° containing compound *and* free $SnCl_4$ (*cf.* b.p. $SnCl_4$, 114°). It would seem that the $SnCl_4 \cdot 2POCl_3$ compound is weak, partly dissociating on distillation, but stronger than the $SnCl_4 \cdot 2SeOCl_2$ compound.

TABLE I

Acceptor	POCl₃	SeOCl₂	CH₃COCl	SOCl₂
CCl₄	No cpd.	Weak cpd.ᵃ	No cpd.	No cpd.
SiCl₄	No cpd.	....	Weak cpds.ᵃ	Weak cpds.ᵃ
AsCl₃	Weak cpd.ᵃ	No cpd.	No cpd.	No cpd.
SnCl₄	Weak cpd.	Weak cpd.	Weak cpd.ᵃ	No cpd.
TiCl₄	2 strong cpd.	Strong cpd.	Weak cpd.	Weak cpd.ᵃ

ᵃ Compound not reported elsewhere in the literature.

(19) G. B. L. Smith, *Chem. Revs.*, **23**, 165 (1938).
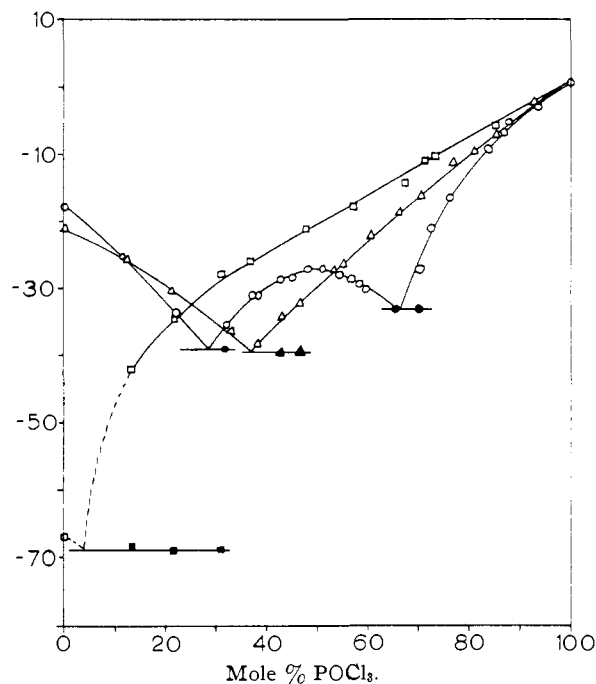
(20) C. R. Wise, THIS JOURNAL, **45**, 1233 (1923).

Fig. 1.— -O-, AsCl₃–POCl₃; -△-, CCl₄–POCl₃; -□-, SiCl₄–POCl₃.
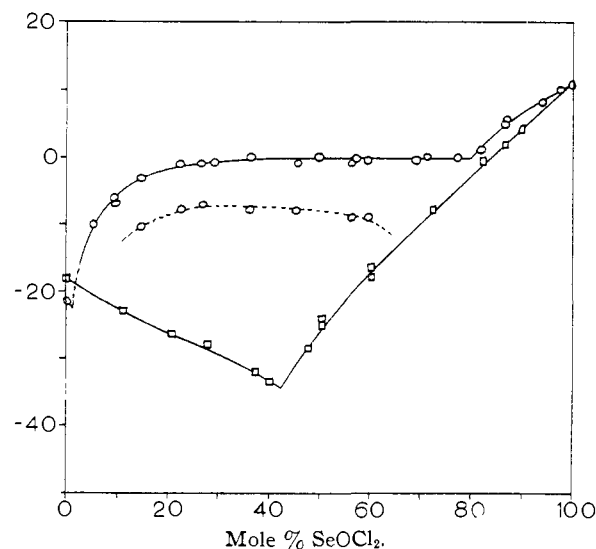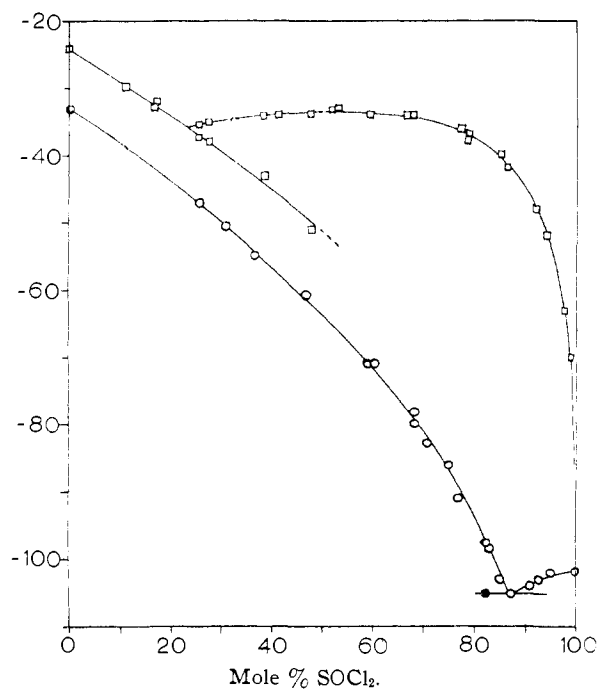

Fig. 2.— -O-, CCl₄–SeOCl₂; -□-, AsCl₃–SeOCl₂.

The cooling curve data reported by Cullinane, *et al.*,[6] for the system $TiCl_4$–CH_3COCl are plotted in Fig. 9 for comparison with our own data. While the curves compare favorably in broad outline, notable lack of agreement can be seen at the extremes of composition. The □ point on the $SnCl_4$–$SeOCl_2$ diagram at *ca.* 90% $SeOCl_2$ is from the solubility data of Wise.[20]

Toward $POCl_3$ the tendency to complex decreases in the order $TiCl_4$, $SnCl_4$, $AsCl_3$, $SiCl_4$ and CCl_4 with no basis for differentiation between CCl_4 and $SiCl_4$. With the exception of three cases, *i.e.*, $SeOCl_2$–CCl_4, $SiCl_4$–CH_3COCl and $SiCl_4$–$SOCl_2$, the same sequence of acceptor strength is observed toward each of the other oxychlorides. It is also seen that the donor strengths of the oxy-
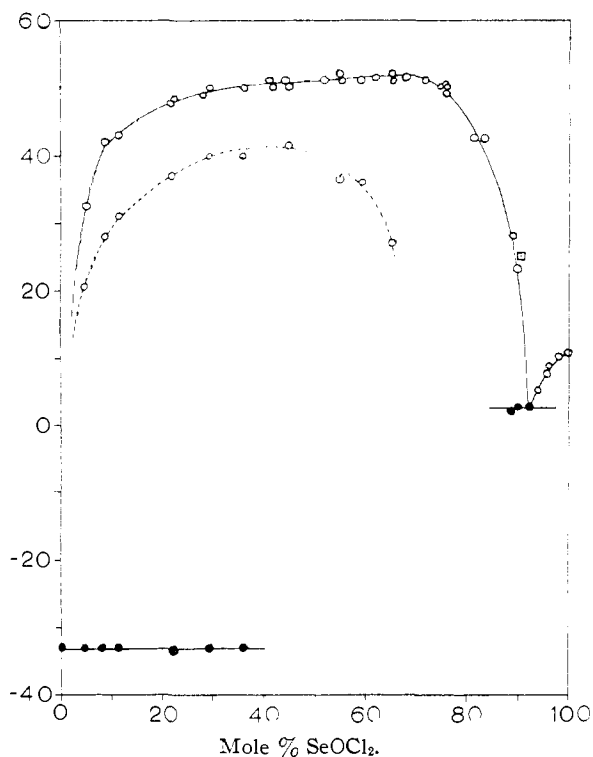
Fig. 3.— -O-, SnCl₄-SeOCl₂.

Fig. 5.— -O-, SnCl₄-SOCl₂;   -□-, TiCl₄-SOCl₂.

Fig. 4.— -O-, AsCl₃-SOCl₂;   -□-, SiCl₄-SOCl₂.

Fig. 6.— -O-, CCl₄-SOCl₂.

chlorides decreases in the order POCl₃, SeOCl₂, CH₃COCl, SOCl₂ and VOCl₃. One former study indicated negligible interaction between SnCl₄ and SOCl₂.[21] We did not expect that the weak
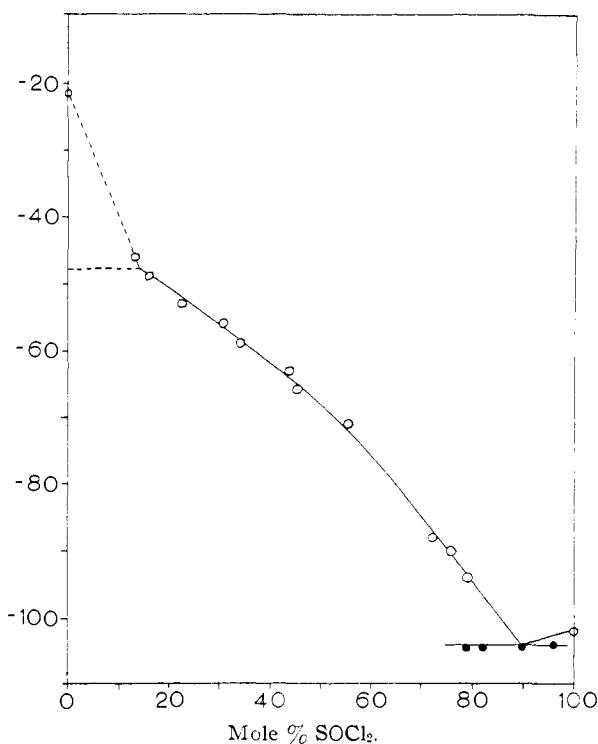
(21) G. H. Locket, *J. Chem. Soc.*, 1501 (1932).

acceptors AsCl₃, SiCl₄ and CCl₄ would give compounds with the weaker donors. However, three exceptions are noted in the SeOCl₂–CCl₄, CH₃-COCl–SiCl₄ and SOCl₂–SiCl₄ systems. It is important to note that the compounds in these cases are entirely dissociated on melting, as witnessed by the extremely flat temperature maxima in the diagrams. In fact it is impossible to decide upon the composition of any of the compounds from the
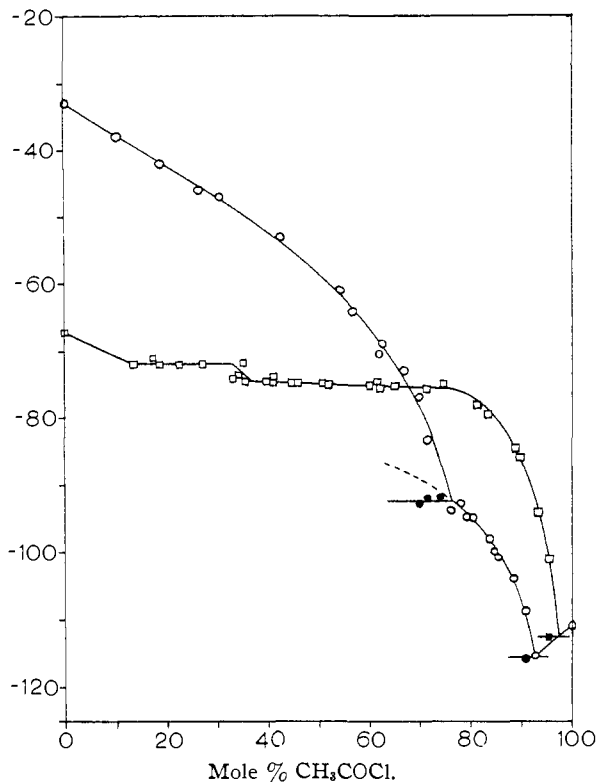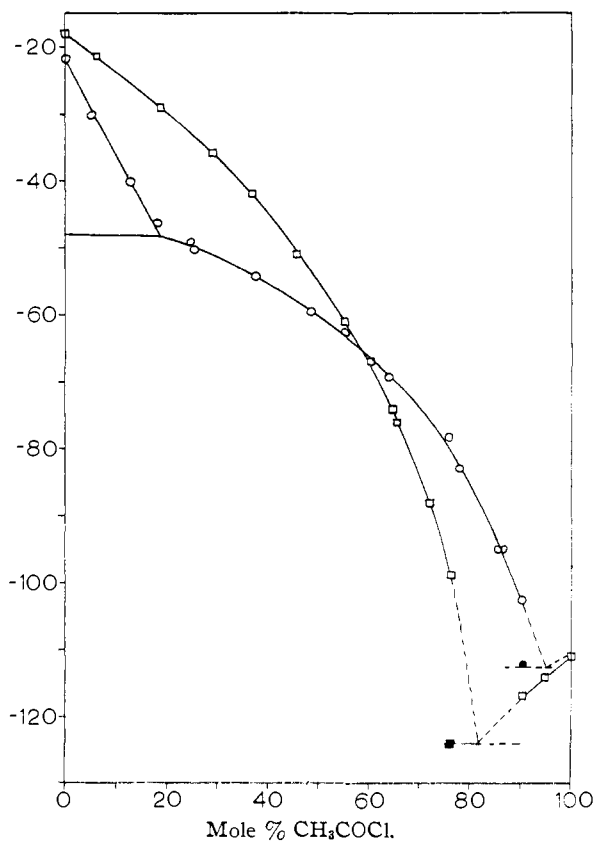
Fig. 7.— -O-, SnCl₄–CH₃COCl; -□-, SiCl₄–CH₃COCl.

Fig. 8.—-O-, CCl₄–CH₃COCl; -□-, AsCl₃–CH₃COCl.

Fig. 9.—TiCl₄–CH₃COCl: -O-, our values; -□-, literature
values.

Fig. 10.—-O-, TiCl₄–VOCl₃; -□-, SnCl₄–VOCl₃.
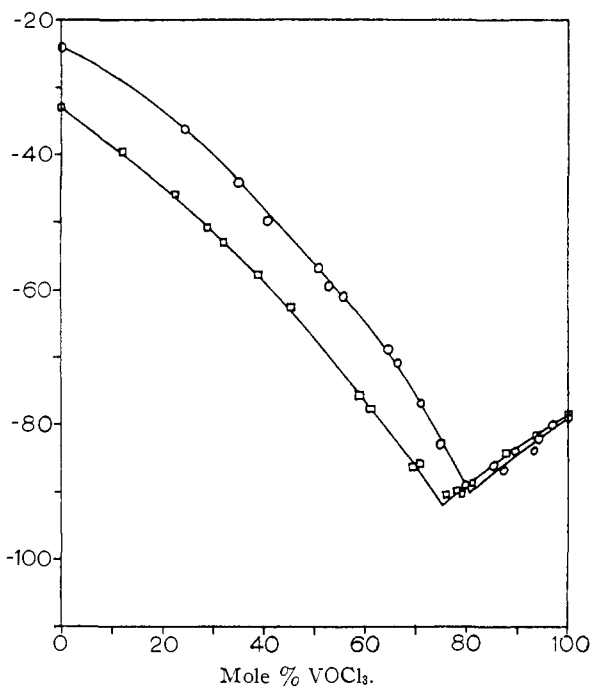
diagrams.   It is possible that the existence of these unexpected compounds is due to convenient crystal packing or dipole interactions.   On the other hand, it is just possible that they are due to donation from SiCl₄ and CCl₄ to the oxychlorides, the latter functioning as acceptors.

Explanation of Donor Strength Sequence.—The bond order of the P–O, Se–O, C–O, etc., bonds in the oxychlorides studied certainly fall between 1 and 2.   For example a phosphoryl compound in which the P–O bond order is one must be designated as $X_3P^+-O^-$.   As electronic charge passes from oxygen to phosphorus the bond order increases.   Similar considerations apply in the Se–O, S–O and C–O bonds.   As a first approximation it might be expected that the greatest electronic charge would reside with the oxygen for that case in

Fig. 11.—-O-, C_5H_5N-$SOCl_2$.

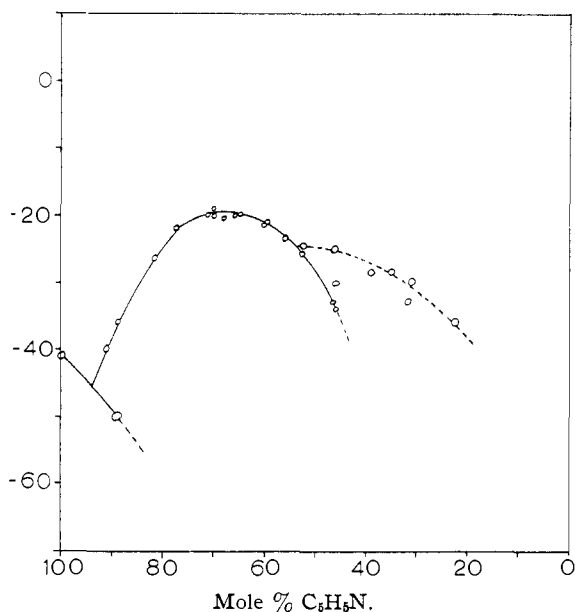which the central atom had the lowest electro-negativity. The "best values" of electronegativity for P, Se, S and C are 2.1, 2.4, 2.5 and 2.5, respectively, according to Pritchard and Skinner.[22] From the above argument the electronic charge on the oxygen atom should be greatest in $POCl_3$ and least (and equal) in $SOCl_2$ and CH_3COCl. If the oxychlorides behave as donors through the oxygen atoms the order of donor strength is explained, since the greater the electronic charge on an oxygen atom the better it is able to act as a donor.

It has been demonstrated in at least two cases, phosphoryl[23] and carbonyl,[24] that the bond order varies with the electronegativities of the other substituent groups on the central atom. Then the above predictions of donor strengths may be refined to account for the effects of other groups around the central atom. From the freezing point diagram data we see that CH_3COCl forms a compound with $SnCl_4$, whereas $SOCl_2$ does not. Also $TiCl_4 \cdot CH_3COCl$ melts some 50° higher than $TiCl_4 \cdot SOCl_2$. These chemical evidences indicate that CH_3COCl is a stronger donor than $SOCl_2$. Such is expected and may be ascribed to the replacement of a chlorine atom on $COCl_2$ by the less electronegative methyl group.

Replacing the other chlorine with a methyl group gives acetone, which should have still stronger donor properties. 1:1 addition compounds of BF_3 with $COCl_2$,[25] CH_3COCl[4] and $(CH_3)_2CO$[26] have been reported to melt at $-134°$, ca. $-70°$ and 35–40°, respectively. Furthermore CH_3COCl forms an addition compound with BCl_3, melting at $-54°$,[7] whereas $COCl_2$ does not form a compounds with BCl_3.[24]

Apparently the attachment of three chlorine atoms to phosphorus in phosphoryl chloride is

(22) H. O. Pritchard and H. A. Skinner, Chem. Revs., 55, 745 (1955).

(23) J. V. Bell, et al., THIS JOURNAL, 76, 5185 (1954).

(24) R. E. Kagarise, ibid., 77, 1377 (1955).

(25) D. R. Martin and J. P. Faust, J. Phys. Colloid Chem., 53, 1255 (1949).

(26) V. Gasselin, Ann. chim. phys., [7] 3, 58 (1894).

insufficient to offset the relatively large difference in electronegativity between P and Se, and $POCl_3$ is the stronger donor of the two.

Tacit in the foregoing discussion is the assumption that the oxygen atom of the oxychloride acts as the donor center. This point has been discussed by us previously,[10] and we believe that the data herein presented are best understood on the same basic assumption. The recent structure determination of $POCl_3 \cdot SbCl_5$ proves that bonding occurs through the oxygen[12] in at least one case.

The application of the above theory to the transition metal oxychloride, $VOCl_3$, is interesting. The donor character of $VOCl_3$ is negligible, as is shown in Fig. 10. The structure of $VOCl_3$ is known to be a slightly distorted tetrahedron,[27] with the V–O bond considerably shorter than the sum of the estimated single bond covalent radii, i.e., 1.56 vs. $1.20 + 0.74$ Å.[27] It is our opinion that such behavior is to be expected in the case of transition elements in which the double bond character involves penultimate d orbitals, lying at energy levels equal to or lower than those used for primary σ-bond formation. It is notable that $VOCl_3$ is not considered an ionizing solvent for $TiCl_4$ or $SnCl_4$, in contrast to $POCl_3$.[28]

Acceptor Properties of the Oxychlorides.—If, as we have assumed, the central atom of an oxychloride bears some positive charge, then it should behave as an acceptor toward sufficiently strong donors. We attempted to obtain the freezing point diagrams of pyridine with each of the oxychlorides. In the cases of $SeOCl_3$ and CH_3COCl chemical reaction takes place when the mixtures are warmed to 100° and above. No accurate diagrams were obtained. 2:1 and 1:1 compounds of pyridine with $SeOCl_2$ have been reported and they decompose upon heating.[29] A 1:1 compound of pyridine with CH_3COCl has been obtained, and it is reported to decompose at 100° also.[30] Zeffert has shown that $POCl_3$ and C_5H_5N form no compound.[31]

The $SOCl_2$-C_5H_5N system, Fig. 11, shows a well characterized 2:1 compound, melting at $-20°$. The low melting point is taken as an indication of weak compound formation. In common with other binary systems where compound formation is weak, metastable solid phases appear often. For example, in the $TiCl_4$-$SOCl_2$ system, $TiCl_4$ solid crystallizes in the region 20–50 mole % $SOCl_2$, where the 1:1 compound is the stable phase, melting at a higher temperature; see Fig. 5. Likewise pyridine crystallizes in the composition range where the 2:1 compound exists in the $SOCl_2$-C_5H_5N system. The latter system exhibits a strong tendency to supercool and form viscous mixtures at low temperatures which defy stirring. However, the 2:1 compound separates fairly readily up to the composition 54 mole % $SOCl_2$. Compositions richer in $SOCl_2$ can be made to crystallize only rarely, and the few freezing points obtained are not in agreement with each other. We believe,

(27) K. J. Palmer. THIS JOURNAL, 60, 2360 (1938).

(28) V. Gutmann and S. Aftalion-Hinl, Monatsh., 84, 207 (1953).

(29) J. Jackson and G. B. L. Smith, THIS JOURNAL, 62, 544 (1940).

(30) V. Prey, Ber., 75B, 537 (1942).

(31) B. M. Zeffert, et al., THIS JOURNAL, 75, 752 (1953).

however, that at least one other solid phase exists in the region 46–76 mole % SOCl₂.

While it is considered that donor–acceptor bonding is responsible for bond formation in most of the cases discussed thus far, it is probable that such bonding is not the only intermolecular attraction in these binary systems, particularly with the more polar POCl₃ and SeOCl₂. We prefer induced dipole–dipole interaction to explain the peculiar diagram obtained for the SnCl₄–SeOCl₂ system. If such interaction became strong enough and the liquid mixture were predominantly non-polar, a second liquid would form containing the SeOCl₂ complex. SnCl₄ is certainly non-polar, but the Sn–Cl bonds must be quite polar. Thus a complex of the nature $Cl_4{}^{\delta-}Sn^{\delta+}\text{-}\overset{-}{O}\overset{+}{Se}Cl_2$ might form, which would be insoluble in SnCl₄. In Fig. 3, the dotted line shows the separation into two liquid phases of supercooled mixtures in the composition range 0–66 mole % SeOCl₂. The heavier phase, on settling, can be made to crystallize and melts at the melting point of the 2:1 compound. The lighter phase crystallizes at a much lower temperature and melts very close to the freezing point of SnCl₄. The metastable liquid phase polar complex would appear to be closely related to the crystalline addition compound; indeed, strong polar interaction would be difficult to distinguish both theoretically and practically from addition compound formation in this system. A similar phenomenon is observed in the SeOCl₂–CCl₄ system, see Fig. 2, although the probable structure here is rather more difficult to postulate.

Infrared Spectra.—The oxygen–central atom stretch frequencies observed under several conditions are given in Table II. Solvent absorption

TABLE II

System	Frequency (cm.⁻¹)	Shift relative to frequency in CS₂ soln. (cm.⁻¹)
POCl₃ in CS₂	1305	.....
POCl₃ in thin film	1300	5
POCl₃ in TiCl₄	1255, 1234	50, 71
POCl₃ in SnCl₄	1265, 1215	40, 90
TiCl₄·2POCl₃ solid	1205	100
TiCl₄·POCl₃ solid	1205	100
SnCl₄·2POCl₃ solid	1300, 1285	5, 20
	1250, 1215	55, 90
SeOCl₂ in CS₂	975	.....
SeOCl₂ in thin film	947	28
SeOCl₂ in TiCl₄	850, 800 (approx.)	
SeOCl₂ in SnCl₄	965	10
TiCl₄·2SeOCl₂ solid	829, 795	144, 180
SnCl₄·2SeOCl₂ solid	947, 835	28, 140

interfered seriously only in the SeOCl₂–TiCl₄ system, which was also unsatisfactory in that the solubility of the addition compound in TiCl₄ is very low. The frequencies given for this system are tentative, but they do show agreement with those observed in the crystalline addition compound. No detectable differences were observed between the stretch frequencies of the pure liquids and their solutions in CS₂, TiCl₄ and SnCl₄ for the compounds CH₃COCl (1820 cm.⁻¹), SOCl₂ (1235 cm.⁻¹) and VOCl₃ (1038 cm.⁻¹).

It is apparent that since no effect upon the

carbonyl, thionyl and vanadyl stretch frequencies is observed, little interaction takes place between these oxychlorides and acceptor molecules. This is consistent with foregoing freezing point diagrams which showed that these three oxychlorides form no compounds with strong acceptors, or, if they do, the components can be distilled apart. Sizable frequency shifts are seen in Table II for the strong donors POCl₃ and SeOCl₂, which we take as an indication that the oxygen atom in each molecule is the donor site. Carbonyl frequency shifts of the same order of magnitude and in the same direction have been observed upon forming addition compounds between ketones and TiCl₄ or BF₃.[32,33] For purposes of this discussion the standard P–O and Se–O frequencies are taken as those found in CS₂ solution. It is also seen in the table that more than one band is attributable to the Se–O or P–O group, particularly under conditions where bonded and non-bonded groups might be expected to be present simultaneously such as a partially dissociated compound. POCl₃ exhibits very similar spectra as the pure liquid and in CS₂ solution. However, two bands are observed when it is dissolved in either SnCl₄ or TiCl₄. The highest frequency band, 1215 cm.⁻¹ in SnCl₄ and 1234 cm.⁻¹ in TiCl₄, can be attributed to the complex in each case as fair agreement exists between these bands and those found for the solid addition compounds. No band is found in the solutions at a frequency near the P–O band of free POCl₃. The second band of lower frequency in each solution might be attributable to a dissociated compound where significant interaction still occurs between the components. It is noteworthy that the solid, SnCl₄·2POCl₃, shows multiple bands. In this case a doublet is found at the frequency of P–O in free POCl₃ in addition to the band at 1250 cm.⁻¹ (*cf.* 1265 cm.⁻¹ for POCl₃ in SnCl₄). The results suggest that some of the POCl₃ molecules in the crystalline compound are not bonded at room temperature through the P–O donor group, nor are they bonded by induced dipole–dipole forces, since the strong band at 1300 cm.⁻¹ is present. The 1250 cm.⁻¹ band in the solid could be due to the same intermolecular forces responsible for the 1265 cm.⁻¹ band in solution. The lowest frequency, 1215 cm.⁻¹, is probably the result of donor–acceptor interaction.

The solid, TiCl₄·2POCl₃, shows a simpler spectrum, one strong band at 1205 cm.⁻¹ with a high frequency shoulder.

Selenium(IV) oxychloride is reported to be an associated substance.[34] The Se–O band in the pure liquid is very broad, but when the compound is dissolved in CS₂, the Se–O band undergoes a shift to higher frequency and the band becomes quite sharp. The most obvious explanation of these facts is that the pure liquid is behaving as donor and acceptor simultaneously. The solid, TiCl₄·2SeOCl₂, shows no bands near that of Se–O in liquid SeOCl₂. Rather two strongly shifted bands are observed. The extent of the shift is such

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(34) W. J. R. Henley and S. Sugden, *J. Chem. Soc.*, 1058 (1929).

as to indicate strong bonding through the oxygen atom. The two bands found for $SnCl_4 \cdot 2SeOCl_2$ indicate strong bonding again through the oxygen atom; but this compound is somewhat weaker than $TiCl_4 \cdot 2SeOCl_2$, in agreement with the observation that the latter can be sublimed whereas the former cannot. The band at 835 cm.$^{-1}$ is weak, the major peak coming at 947 cm.$^{-1}$. The latter frequency is characteristic of liquid $SeOCl_2 \cdot$ $SeOCl_2$ dissolved in $SnCl_4$ exhibits only one band which is but slightly shifted from the standard frequency, from which we can conclude that very little interaction between the components of the solution takes place. However, it appears that $SeOCl_2$ interacts strongly with $TiCl_4$ when the latter is used as solvent for the former.

In the liquid systems it is to be noted that the intensity of the most strongly shifted band (the one we postulate as being due to donor–acceptor interaction) is reduced relative to the intensities of other bands observed in the order $POCl_3$–$TiCl_4$, $POCl_3$–$SnCl_4$, $SeOCl_2$–$SnCl_4$, a strongly shifted band being absent in the last system. The order follows the degree of donor–acceptor action postulated in Table I. It is possible that similar spectral studies could be used to measure the degree of association of molecular complexes in the liquid state.

CHAPEL HILL, N. C.

Effects of Surface Active Substances on Polarographic Waves of Copper(II) Ions[1]

BY I. M. KOLTHOFF AND Y. OKINAKA

A study has been made of the effects of anionic, non-ionic and cationic surface-active substances on the polarographic waves of copper(II) ions in non-acidified and acidified solutions. The reduction of copper(II) ions in 0.1 M perchloric acid is irreversible but is made more reversible by the presence of anionic surface-active substances. Non-ionic and cationic surface-active substances distort the copper wave, the effect of cationic substances being much greater than that of non-ionic substances. With several uncharged and cationic substances two waves are observed, the first wave being kinetic in nature both in acidified and non-acidified solutions. The kinetic current in acidified solutions is controlled by the rate of penetration of aquo-copper(II) ions (penetration current) through the adsorbed film of surface-active substance in accordance with Frumkin's theory. In non-acidified solutions or in fluoride buffers of pH 4.5 to 5 containing Triton X-100, a kinetic current is observed which is much larger than that in acidified solutions. This current is the sum of the penetration current of aquo-copper(II) ions and a kinetic current attributed to a two electron reduction of $CuOH^+$, the formation of which at the electrode surface is controlled by the rate of the reaction $Cu^{+2} + OH^- \rightarrow CuOH^+$. It appears that the rate of this reaction is dependent upon the nature of the surface-active substance present in the system.

Surface-active substances (denoted as SAS) usually employed to eliminate maxima on polarographic waves often cause undesirable effects such as suppression of a diffusion current, shift of a half-wave potential, splitting of a wave into two or more waves or a combination of these effects. No general interpretation is found in the literature, although several examples of these effects are described. Lingane[2] was the first to describe the effect of gelatin on the copper wave in solutions acidified with sulfuric acid, but no interpretation was given. Tanford[3] reported that the copper wave becomes increasingly more distorted with decreasing pH in the presence of serum or egg albumin and interpreted this result in terms of an electrostatic repulsion between copper ions and positively charged protein molecules at low pH values. Kivalo[4] also studied the same phenomenon but attributed the greater distortion at lower pH to a stronger adsorption of the protein molecules on the mercury surface at lower pH values. Effects of other SAS's on the copper wave also have been described by several authors,[5] but no systematic

studies are described on the effect of charge type of an SAS on the appearance of the current-potential curves in acidified and non-acidified media.

In the present paper results of such a study are described and discussed. The experiments were carried out in the presence of sufficiently large amounts of SAS to assure complete coverage of the mercury surface by the adsorbed substance from the beginning of the drop formation, so that the effect of adsorption kinetics on polarograms need not be considered.

Experimental

Materials.—Reagent grade sodium perchlorate was recrystallized twice from conductivity water, dried first in a vacuum desiccator and finally in an oven at 110°. Other chemicals were used without further purification. The copper content of the stock solution of copper perchlorate was determined iodometrically. A stock stolution of dodecylamine perchlorate was prepared by dissolving 0.5 gram of Armeen 12D (Armour and Co.)[6] in 100 ml. of a standard perchloric acid containing the equivalent amount of the acid. The pH of this solution was found to be equal to 6. Sodium dodecyl sulfate was a product of Proctor and Gamble Co. Igepon AP Extra (fatty alkyl ester sulfonates) was obtained from General Dyestuff Corporation. Samples of

(1) This investigation was supported by a research grant from the National Science Foundation.

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(6) Dodecylamine 95%, tetradecylamine 3%, decylamine 2%; average molecular weight, 185.