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# Radiochlorine Exchange Reactions in Sulfur Monochloride[1]

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Chloride lability in the solvent sulfur monochloride has been investigated by studying radiochlorine exchange rates between the solvent and the four solutes tetraethylammonium chloride, antimony tri- and pentachlorides, and thionyl chloride. Exchange is rapid and complete in the first three cases and, at best, very slow in the last. The results suggest a ready dissociation of solvent chloride in the presence of (and only in the presence of) a strong chloride acceptor, none being evident with thionyl chloride. It is inferred that the ready exchange observed with the ionic substance, tetraethylammonium chloride, probably goes *via* a bimolecular process or an association equilibrium. The experiments appear to imply a limited general importance for chloride dissociation in this medium.

The use of isotopic tracers has helped materially to clarify our understanding of such features of nonaqueous medium chemistry as solvent ion lability and the probable importance of various postulated ionic acid–base equilibria, tending in some cases to support (although not always unambiguously) such postulates[3] and in others not to do so.[4] In extension of such work, it seemed inviting to study the nonaqueous solvent sulfur monochloride, a substance recently investigated (following earlier treatment by Walden[5]) from a solvent systems viewpoint by Spandau and Hattwig.[6] Previous work has shown chlorine exchange between hydrogen chloride and sulfur monochloride[7] and sulfur exchange between dissolved sulfur and sulfur monochloride[8] both to be slow, but experiments seemed desirable more specifically directed toward providing an indication of solvent ion lability and the probable significance of its self-ionization and/or ionic acid–base interactions with solutes. This paper reports results of exploratory studies of radiochlorine exchange rates between the solvent and acid and basic chloride solutes.

## Experimental

The procedures in general involved standard high-vacuum techniques. All moisture-sensitive substances were handled either in the vacuum system or sometimes in a drybox. Stopcocks exposed to sulfur monochloride, antimony pentachloride, or thionyl chloride were lubricated with Halocarbon[9] grease, found quite resistive to them, and no exposure of experimental substances to mercury occurred in the work. Transfers of these volatile materials were effected by distillation with liquid nitrogen. For radioassay, the tracer used, chlorine-36, was, as before,[3b] precipitated as mercurous chloride and counted on cupped stainless steel planchets under an end window Geiger counter, normally in duplicate and sufficiently long to minimize statistical effects, background and self-absorption corrections being applied.

**Materials.**—Chlorine-36 was obtained from the Oak Ridge National Laboratory as a hydrochloric acid solution (Item Cl-36-P) and was used as such for labeling purposes.

Sulfur monochloride (Matheson Coleman and Bell, practical) was purified by a double distillation from small amounts of sulfur and charcoal[10] (Norit) into liquid nitrogen cooled receivers, first at somewhat reduced pressure with slight heating and then under high vacuum without heat. About the middle two-thirds was collected each time. The golden yellow product was stored in sealed ampoules containing small amounts of sulfur and charcoal. Before each experiment the first portion of the distillate from the stock supply being used was discarded. Labeled sulfur monochloride (specific activity, 15.6 c.p.m./mg., as mercurous chloride) was obtained by exchange of the solvent with labeled tetraethylammonium chloride (an exchange found fast in this research).

Tetraethylammonium chloride hydrate (Reagent, K. and K. Laboratories, Inc.) was activated, following Herber,[11] by exchange in water with labeled hydrochloric acid. After evaporation to dryness, the salt was dried under high vacuum at 115° overnight, recrystallized from acetone, again dried in a like manner, and finally stored over phosphorus pentoxide. (Specific activity, 2607 c.p.m./mg.) *Anal.* Calcd. for $(C_2H_5)_4NCl$: Cl, 21.26. Found: Cl, 21.39.

Antimony trichloride (Baker, analyzed) was activated by the exchange (not previously observed) with active potassium chloride (itself activated by exchange with labeled hydrochloric acid). The dried potassium chloride was dissolved in the trichloride just above its meting point (giving a dark reddish brown solution), and then the trichloride was distilled off, about the middle two-thirds being collected and stored, after solidification, over phosphorus pentoxide. On the basis of the rather approximately known initial hydrochloric acid activity, the final specific activity of 509.0 c.p.m./mg. was estimated to correspond, at least roughly, to a probably complete exchange.

Labeled antimony pentachloride was prepared by oxidation of labeled trichloride with gaseous chlorine. The product was distilled in the vacuum system, the middle half being retained. (Specific activity, 210.2 c.p.m./mg.) *Anal.* Calcd. for $SbCl_5$: Cl, 59.28. Found: Cl, 59.63.

Thionyl chloride (Matheson Coleman and Bell, practical) was refluxed with raw linseed oil and then distilled from the mixture

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[2] Taken from the M.S. thesis of Ronald R. Wiggle, at Oregon State University, Aug., 1963.

[3] For example: (a) J. Lewis and R. G. Wilkins, *J. Chem. Soc.*, 56 (1955); (b) B. J. Masters, N. D. Potter, D. R. Asher, and T. H. Norris, *J. Am. Chem. Soc.*, **78**, 4252 (1956); (c) L. F. Johnson, Jr., and T. H. Norris, *ibid.*, **79**, 1584 (1957).

[4] For example: (a) E. C. M. Grigg and I. Lauder, *Trans. Faraday Soc.*, **46**, 1039 (1950); (b) R. Muxart, *Compt. rend.*, **231**, 1489 (1950); (c) R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Am. Chem. Soc.*, **73**, 3052 (1951); (d) J. L. Huston, *J. Inorg. Nucl. Chem.*, **2**, 128 (1956); (e) J. L. Huston and C. E. Lang, *ibid.*, **4**, 30 (1957); (f) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 1305 (1963).

[5] P. Walden, *Z. anorg. allgem. Chem.*, **25**, 209 (1900).

[6] H. Spandau and H. Hattwig, *ibid.*, **311**, 32 (1961).

[7] K. Clusius and H. Haimerl, *Z. physik. Chem.*, **B51**, 347 (1942).

[8] (a) R. A. Cooley and D. M. Yost, *J. Am. Chem. Soc.*, **62**, 2474 (1940); (b) A. Fava and L. Salsilli, *Ricerca sci.*, **24**, 275 (1954).

[9] Halocarbon Products Corp., Hackensack, N. J.

[10] F. G. Mann, W. J. Pope, and R. H. Vernon, *J. Chem. Soc.*, **119**, 634 (1921).

[11] R. H. Herber, *J. Am. Chem. Soc.*, **80**, 5080 (1958).

through a packed column (all at atmospheric pressure), about the middle two-thirds being collected. This product was then distilled *in vacuo*, about the middle three-quarters being further fractionated by a double passage through four successively colder traps, the material retained in the two middle traps (−45.2 and −83.6°) being taken each time, first for a second passage through the traps, and then as the final, completely colorless product.[12] Labeled thionyl chloride was prepared *via* the rapid exchange of the liquid from the first distillation with labeled tetramethylammonium chloride[3b] (itself labeled in essentially the same way as tetraethylammonium chloride). Repeated fractionation of the product *in vacuo* through cold traps, as with the inactive substance, yielded a colorless product (specific activity, 43.4 c.p.m./mg.).

**Run Procedure. Exchange with Tetraethylammonium Chloride.**—A small, weighed quantity of well-dried, labeled solute was dissolved at 0° in a measured portion of solvent with vigorous stirring (ice bath and Teflon-covered magnetic stirring bar). As soon as solution was substantially complete (the solubility is limited), a sample of the solvent was taken by evaporation over an interval of several seconds, and then, over several minutes, periodic further similar vapor samples were taken; zero time was recorded as that of the first solute–solvent contact. Finally, in one of the two experiments, the residual solution was sampled with a pipet to obtain an indication of the average specific activity of the solution (the vapor samples' drain having been very small) and hence of the expected infinite time specific activity ($S_{\infty \text{ expt}}$); comparison of this quantity with the infinite time specific activity calculated from the known amounts of reactants, together with the initial solute activity ($S_{\infty \text{ calcd}}$), provided a useful and satisfactory check (the two quantities being within 2%) of the experimental procedure. The apparent percentage exchange, $100F$, for each vapor sample was calculated from the observed specific activity of that sample ($S$) thus: $F = S/S_\infty$. The quantity $S_{\infty \text{ calcd}}$ was used for the reported figures (little different from those based on $S_{\infty \text{ exptl}}$). In order to obtain these specific activities, the samples (vapor or solution) were hydrolyzed in dilute base, then oxidized with 30% hydrogen peroxide. Some free sulfur was removed manually, excess peroxide was destroyed by heat and then boiling of the acidified solution, and sulfate was eliminated by precipitation with barium nitrate. Finally mercurous chloride was precipitated by addition of the nitrate to the acid solution. For counting, this material, centrifuged and washed, was slurried in acetone and plated onto cupped, stainless steel planchets, with drying under a heat lamp.

**Exchange with Antimony Tri- and Pentachlorides.**—Here the technique was substantially as above. The pentachloride was dosed as liquid in the vacuum system, instead of by weight. Arrangements were made for introducing the solutes (labeled) rapidly into the solvent. (A deepening of color occurs in both cases, suggestive of complex formation.) The residual solution samples, after acid hydrolysis, were freed of antimony by sulfide precipitation before further treatment to precipitate sulfate and finally mercurous chloride. As a precaution against incomplete reactant separation, the solvent vapor samples from the pentachloride experiments, where the solute, though less volatile than the solvent, was not negligibly so, were further fractionated by distillation from a −22.9° bath into liquid nitrogen. Agreements between apparent percentage exchanges based on $S_{\infty \text{ calcd}}$ and $S_{\infty \text{ exptl}}$ were reasonably satisfactory, although somewhat less so with the pentachloride, probably consequent to dosing difficulties with this substance. The latter, probably more reliable, figures have, therefore, been reported here.

**Exchange with Thionyl Chloride.**—Here two techniques were used. In the first, the sulfur monochloride was initially labeled, and a relatively modest excess over solute was used. The reactants were dosed and brought rapidly together in the vacuum system, and then, periodically, samples (primarily thionyl chloride) were evaporated from the solutions. These samples, heavily contaminated with solvent, were fractionated through successively colder traps (−22.9 to −63.5°) into liquid nitrogen, the material reaching the latter trap being taken as a "thionyl chloride" fraction. This fractionation was only moderately successful, as evidenced by a yellow tinge in the samples, by the erratic results, and by the finding of a significant apparent zero time exchange (despite the apparent occurrence of no further exchange). Nevertheless, the results are certainly meaningful. The fractions were hydrolyzed in water, boiled to expel sulfur dioxide, then treated as before, first to eliminate sulfate (from sulfur monochloride contamination), then to precipitate mercurous chloride for counting. The apparent percentage exchange was calculated from the resulting "thionyl chloride" fraction specific activity, $S$, thus: $F = S/S_\infty$, where $S_\infty$ was calculated from the initial solvent activity together with the known relative reactant quantities. Finally, in the long term experiment, the solution was evaporated to ~10% volume to eliminate the bulk of the thionyl chloride, and the resulting sample was hydrolyzed and counted to give a solvent specific activity, $S_b$. Comparison with the initial activity, $S_{b(0)}$, gave an alternative (and probably more reliable) basis for apparent per cent exchange calculation: $F = [S_{b(0)} - S_b](a + b)/[S_{b(0)}]a$ ($a$ and $b$ are equivalents of $SOCl_2$ and $S_2Cl_2$, respectively).

In the second procedure, an effort was made to achieve better reactant separation. Here thionyl chloride was initially labeled and the reactants were separated into two fractions on the basis of their markedly different hydrolysis rates in water at 0°, sulfur monochloride being physically separable from the solution formed by the rapidly hydrolyzed thionyl chloride. Treatment of the separate fractions as before led to specific activities ($S_a$ for $SOCl_2$, $S_b$ for $S_2Cl_2$) from which apparent percentage exchanges were calculated: $F = S_b(a + b)/[S_bb + S_aa]$, $a$ and $b$ again representing $SOCl_2$ and $S_2Cl_2$ equivalents. Although the separation seemed effective, the observation of an apparently substantially complete exchange directly conflicts with the results of the first procedure, and we must conclude that catalysis of the exchange probably occurs during the separation. Hence the results here must be discounted.

## Results

**Exchange with Tetraethylammonium Chloride.**—Two experiments were done, both at 0°, with respective solute mole fractions of 0.0031 and 0.0042. Samples were taken at: (1) 2, 5, 10, and 20 min.; (2) 2, 5, 8, and 14 min. The observed apparent exchanges from these samples were, in order: (1) 102, 103, 103, and 100%; (2) 98, 100, 102, and 98%. Clearly the exchange is rapid and complete, and no trend in the figures with time is evident. An estimated maximum half-time would be about 0.4 min.

**Exchange with Antimony Trichloride.**—Two experiments were done, both at 0°, with respective solute mole fractions of 0.0115 and 0.0118. Samples were taken at: (1) 1, 5, 10, and 20 min.; (2) 0.5, 5, 10, and 20 min. The observed apparent exchanges from these samples were, in order: (1) 99, 111, 100, and 96%; (2) 87, 106, 106, and 106%. Again the exchange is clearly rapid and complete, no trend in the figures with time being evident. An estimated maximum half-time would be about 0.2 min.

**Exchange with Antimony Pentachloride.**—Two experiments were done, at 0°, both with solute mole fractions of 0.0186. Samples were taken at: (1) 0.5, 4, and 6.5 min.; (2) 0.5, 3, 7, and 10 min. The observed apparent exchanges were, in order: (1) 101, 102, and 99%; (2) 101, 100, 100, and 99%.

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[12] Thanks are due to Mr. Ralph L. Bain of this laboratory for help with this purification.

Once more the exchange is evidently rapid and complete. An estimated maximum half-time would be about 0.1 min.

**Exchange with Thionyl Chloride. (a) Vacuum Fractionation Procedure.**—Experiments were done at (1) −22.9° and (2) 25°, with thionyl chloride mole fractions, respectively, of 0.302 and 0.305. In (1) the fractionated "thionyl chloride" samples, taken at 0.5, 3.5, 7.3, and 10.3 min., gave the apparent fraction exchanges 9, 9, 89, and 10%, respectively. In (2) similar samples, at 1 and 2 min. and 2, 6, 14, 24, and 48 hr., gave the apparent exchanges 43, 76, 20, 34, 19, 35, and 44%, respectively. Finally, in (2), the activity of the residual solvent after evaporation of most of the solution indicated an apparent exchange at 48 hr. of 13 ± 5%. The erratic results are unquestionably attributable to irreproducible and incomplete separations. However, they certainly show no clearly progressing exchange and hence definitely show the exchange here, unlike the others studied, to be, at best, quite slow. Probably the most reliable figure, quantitatively, is the last recorded, where the separation of reactants should have been relatively adequate. On the basis of this figure one may estimate a minimum half-time at 25° of 100 hr. In view of the scatter of the data, however, it seems quite possible that the true half-time is far longer.

**(b) Hydrolysis Separation Procedure.**—Experiments (thionyl chloride mole fraction 0.313) were done at (1) 0°, (2) −45.2°, and (3) −83.6°, the times being, respectively, 5, 5, and 1 min. The observed apparent exchanges were 91, 101, and 89%, respectively. Complete and rapid exchange is clearly suggested. However, these results equally clearly are in direct conflict with those involving the vacuum fractionation procedure. Hence we conclude that a separation procedure induced exchange has occurred, and the results are to be discounted.

## Discussion

The experiments show a ready lability of solvent chloride ions in the presence of either the basic chloride solute, tetraethylammonium chloride, or the acids (*i.e.*, chloride acceptors), antimony tri- or pentachloride. On the other hand, in interesting contrast, one finds no evidence of such lability in the presence of the solute, thionyl chloride, a substance of less obviously pronounced chloride donor or acceptor character.

Thus the evidence appears consistent with a ready dissociability of solvent chloride, at least in the presence of a strong chloride acceptor solute, equilibria of the sort suggested by Spandau and Hattwig[6] quite possibly operating, *e.g.*

$$SbCl_3 + S_2Cl_2 \rightleftarrows S_2Cl^+ + SbCl_4^-$$

In the case of antimony pentachloride, it seems likely that an analogous equilibrium prevails, any reaction leading to a complex such as $SCl_4 \cdot SbCl_5$, as described by Partington,[13] probably being significantly slower. The thionyl chloride result suggests, however, that, in the absence of a strong chloride acceptor, no such ready solvent chloride dissociability operates. This follows since previous[3b,c] as well as more recent[14] research in this laboratory has provided evidence for a ready chloride dissociability on the part of thionyl chloride. Thus the nonrapid exchange in the present system stands sharply in contrast to the fast exchange observed between thionyl chloride and thionyl bromide,[3c] a result assumed attributable to the ready dissociation of both species involved. On the other hand, we find here a definite parallel to Lewis and Sowerby's observation of only a slow chloride exchange between nitrosyl chloride and phosphorus oxychloride,[15] a result attributed to a lack of dissociation tendency for phosphorus oxychloride, somewhat analogous to the situation here with sulfur monochloride.

Thus one concludes that any self-ionization in this medium (conductance measurements suggest it to be very slight[16]) must be, at best, of minor kinetic significance. This point is of some relevance in the interpretation of the rapid exchange observed between the solvent and tetraethylammonium chloride. One is led to believe that this exchange probably occurs *via* a direct solvent–chloride ion interaction, either a mobile association equilibrium or a bimolecular process analogous to that shown by Lewis and Sowerby probably to operate in the analogous exchange with phosphorus oxychloride.[17]

The experiments show, then, the chloride dissociation tendency in this solvent to be of only limited importance, a situation seemingly aligning it somewhat more closely in this respect with the solvents phosgene[4d,e] and phosphorus oxychloride[4f,17] (even though it does exchange readily with acid solutes, in contrast to these solvents) than with substances such as thionyl chloride or nitrosyl chloride.[3a]

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(17) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957).