

ADSORPTION CHROMATOGRAPHY ON CELLULOSE

VIII. THE BEHAVIOUR OF SbCl_5
IN VARIOUS CHROMATOGRAPHIC SYSTEMS

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In a previous paper¹, the remarkable increase in the adsorption of gold(III) halides on cellulose when chromatographed with mineral acids such as H_2SO_4 or H_3PO_4 was described. The phenomenon could not be elucidated with the results obtained with Au(III) halides and it was hoped that work with other halides which also adsorb strongly on cellulose would provide further evidence.

Unfortunately few halogeno-complexes are suitable for such studies². Ga(III) and Po(IV) adsorb only from solutions containing high concentrations of HCl. There remained Sb(V) which in our studies gave consistently two spots due to the presence of hydrolysed species as well as HSbCl_6 .

Thus, in order to study the adsorption of HSbCl_6 from, for example, H_2SO_4 solutions, a knowledge of the general solution chemistry and chromatographic behaviour of HSbCl_6 had to be obtained. The literature on the solution chemistry of HSbCl_6 consists of a detailed spectrophotometric study of equilibrium conditions and kinetics of hydrolysis^{3,4} and a series of contradictory statements concerning the chromatographic behaviour. NEUMANN³ claims that Sb(V) in HCl is not adsorbed on cation exchangers, while KRAUS *et al.*⁵ use this very adsorption on Dowex-50 to effect separations of Sb(V) from other elements. The work of NEUMANN³ shows clearly that a series of chloro-hydroxy complexes exist in all but 12 N HCl solutions and these have even yielded multiple spots in paper chromatography (MATSUURA⁶), while KRAUS AND NELSON⁷ note one single species of Sb(V) in all concentrations of HCl in their study of the adsorption of metal ions on Dowex-1.

In our previous work on the adsorption of Sb(V) on cellulose we had observed two spots when working with Sb(V) obtained by oxidising Sb(III) in HCl². In the present work we improved on the experimental conditions by replacing Whatman No. 1 paper by the thicker Whatman No. 3MM which permits chromatography with conc. HCl and by using pure SbCl_5 as the starting product.

By carrying out "progress chromatograms" with solutions of SbCl_5 in various concentrations of HCl in water, confirmation (although qualitative) of the spectrophotometric work of NEUMANN³ was obtained. In very dilute HCl (3 N and 1 N) the hydrolysis of HSbCl_6 is considerably slower than expected, compared to higher con-

centrations, but this is also in agreement with the kinetic studies of NEUMANN⁴ on the effect of H⁺ ions on the speed of hydrolysis.

Partition and ion exchange chromatograms carried out with solutions of varying degree of hydrolysis were then considered. Paper chromatography with butanol-6 *N* HCl or butanol-3 *N* HCl yields essentially the same chromatograms irrespective of the starting solution used, thus suggesting considerable alteration of the complexed state during development with organic solvents. The slow-moving spot described by MATSUURA⁶ was absent in these chromatograms although we had observed it on previous occasions with solutions of Sb(V) which were obtained by oxidation of Sb(III). This would indicate that the slow-moving spot is possibly due to polymers formed when oxidation is carried out in dilute HCl, since the simple hydroxy-chloro complexes are present in our solutions.

Ion exchange studies with Whatman anion exchange resin paper yielded a good resolution of the various chloro-hydroxy Sb(V) ions, giving good correlation with the spectrophotometric results of NEUMANN³.

From the above studies it was evident that during a chromatographic run of about 20 to 40 min a complete hydrolysis of HSbCl₆ does not occur even in very dilute HCl. Several days are necessary for the complete decomposition of HSbCl₆ in 1 *N* HCl. Thus unless an unlikely specific catalytic effect is exerted by aqueous H₂SO₄ or H₃PO₄ on HSbCl₆, any increase of adsorption due to these acids in the developing solvent must indicate the formation of compounds between these acids and HSbCl₆ in a way which does not involve the loss of a chloro-group from the coordination shell of the Sb(V). As is shown in the experimental part, there is a marked increase of adsorption from mixtures of HCl-H₂SO₄ as well as from either H₂SO₄ or H₃PO₄.

EXPERIMENTAL

(1) *Studies with solutions of SbCl₅ in HCl by adsorption chromatography on cellulose*

Solutions of SbCl₅ in HCl were prepared by adding 1 ml of pure SbCl₅ (Carlo Erba, Milano) to 100 ml of HCl of the required strength at room temperature (17 ± 1°). Solutions in 100%, 90%, 80%, 70%, 60%, 30% and 10% conc. HCl were prepared. The solution in 10% HCl yields a bulky white precipitate while the others form clear solutions, which have a straw-coloured tint in higher concentrations of HCl.

Fig. 1 shows a progress chromatogram of the solutions from 100% to 60% conc. HCl being chromatographed several minutes, 2 h, 17 h and 24 h after addition of the SbCl₅ to the HCl solutions. 50% aqueous HCl was used as solvent. The solution in conc. HCl yields a faint forward trail with this developing solvent; however, since the concentration of HCl is below that of all the solutions in which hydrolysis is being followed, the reconversion of hydrolysed species into HSbCl₆ cannot occur.

In Fig. 2 some results with solutions of SbCl₅ in 30% and 10% HCl are shown using 30% HCl as developing solvent. Even in 30% HCl, HSbCl₆ shows little tendency to hydrolysis during development. It is interesting to note that the HSbCl₆ spot will still be obtained from solutions in 10% HCl for several days.

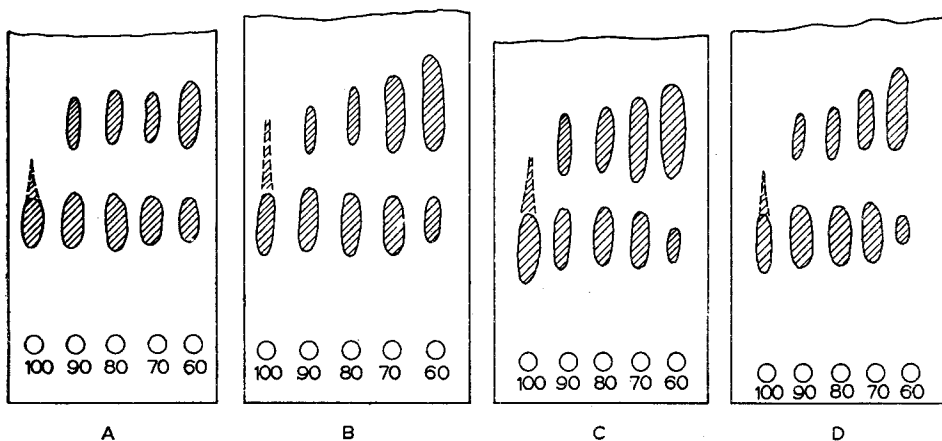


Fig. 1. A progress chromatogram of pure SbCl_5 dissolved in conc. HCl, 90%, 80%, 70% and 60% aqueous HCl. Paper: Whatman No. 3 MM; solvent 50% aqueous HCl. The spots are revealed by spraying with an aqueous KI solution. (A) Chromatographed a few minutes after adding SbCl_5 to the HCl solution; (B) the same solutions 2 h later; (C) the same solutions after standing 17 h; (D) after 24 h.

The R_F value of the hydrolysed species increases in the dilute HCl solutions but not enough to permit a separation from the slower hydrolysed species.

(2) Partition chromatography

The five solutions chromatographed in Fig. 1 were run on Whatman No. 3MM paper with butanol-3 *N* HCl and butanol-6 *N* HCl (equal volumes). In butanol-3 *N* HCl all solutions gave a spot at R_F 0.52 (with reference to the solvent front) another at 0.79 (on the acid front) and a third spot on the solvent front. The spot on the solvent front is strongest with SbCl_5 in conc. HCl. In butanol-6 *N* HCl all solutions gave a double

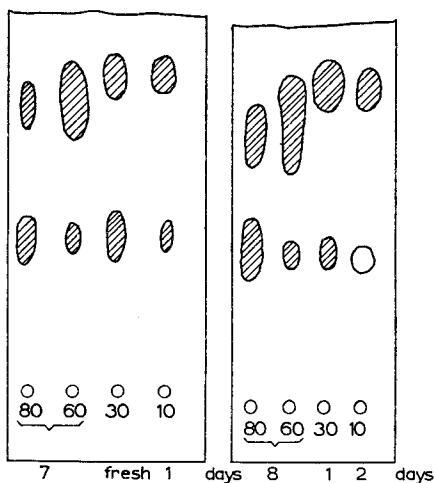


Fig. 2. Chromatograms of solutions of SbCl_5 (1:100) in aqueous 80%, 60%, 30% and 10% HCl. The age of the solutions is given in the figure.

spot on the liquid front and just below it. Owing to this establishment of equilibrium in the organic solvent, partition chromatography seems unsuitable for analysing solutions of SbCl_5 in HCl .

(3) *Ion exchange chromatography*

Whatman "Weak Anion Resin Loaded Paper" kindly supplied by its manufacturers was used, and development was carried out by the ascending method. Fig. 3 shows some of the results with 50% and 30% HCl as developer. If these are compared with

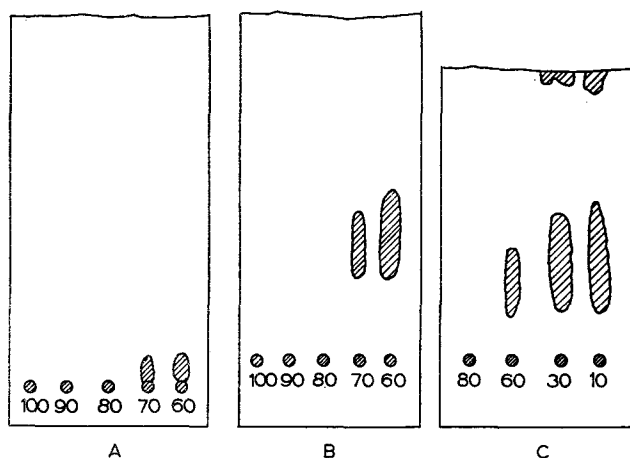


Fig. 3. Chromatograms of aged solutions of SbCl_5 in HCl (concentrations given under each chromatogram in the figure) on Whatman "Weak Anion Resin Loaded Paper". (A) With 50% HCl as solvent, (B) and (C) with 30% HCl as solvent.

the separations on cellulose paper and/or the results obtained by spectrophotometry³ it is obvious that both HSbCl_6 and HSb(OH)Cl_5 are strongly retained at the origin. $\text{HSb(OH)}_2\text{Cl}_4$ moves with an R_F of 0.36 (approximately) in 30% HCl and only 0.04 in 50% HCl . Hence also for this species the adsorption is not one of ion exchange, otherwise adsorption would have to be stronger with a more dilute HCl solution. In aged solutions of SbCl_5 in 30% and 10% HCl , another spot at the liquid front can be detected which could evidently be due to $\text{HSb(OH)}_3\text{Cl}_3$ and more hydrolysed species. It is thus possible to detect HSbCl_6 on cellulose paper, and to separate mixtures of hydrolysed species into three groups on resin-loaded paper.

(4) *The effect of H_2SO_4 and H_3PO_4 on the adsorption of HSbCl_6 on cellulose*

HSbCl_6 in conc. HCl was studied throughout, as this was shown to contain practically pure HSbCl_6 without hydrolysis products.

Fig. 4 shows the R_F values obtained when mixtures of HCl and H_2SO_4 are used as developing solvent, and these are compared with the R_F values in aqueous HCl . Even in water, $N/10$ and $N/2$ HCl no extensive decomposition of the HSbCl_6 spot could be observed in a 10 cm run which requires about 20 min, although a forward comet

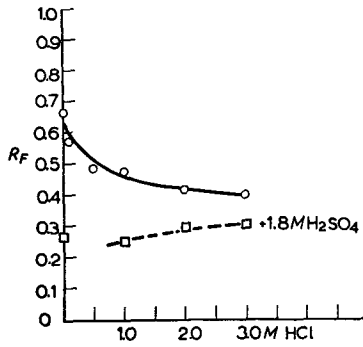


Fig. 4. The R_F values of HSbCl_6 (in conc. HCl) developed with HCl or mixtures of 1.8 M H_2SO_4 -HCl.

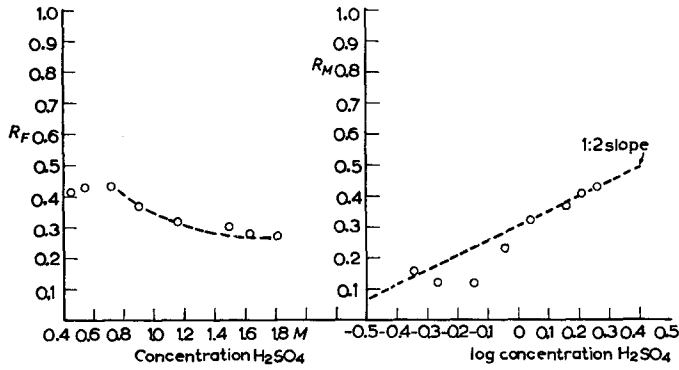


Fig. 5. R_F -concentration H_2SO_4 and R_M -log concentration H_2SO_4 relationships for HSbCl_6 developed with aqueous H_2SO_4 .

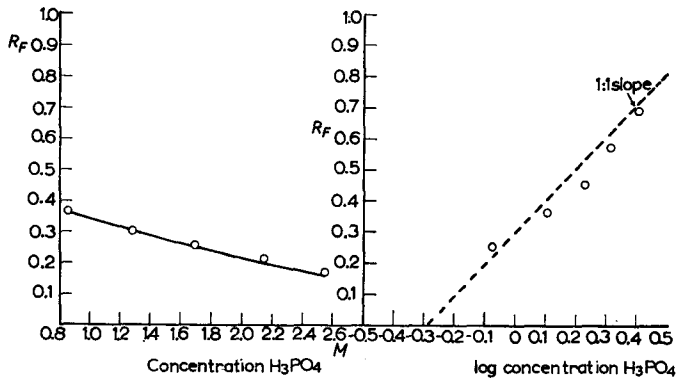


Fig. 6. R_F -concentration H_3PO_4 and R_M -log concentration H_3PO_4 relationships for HSbCl_6 developed with aqueous H_3PO_4 .

and sometimes a faster spot clearly indicates that hydrolysis products are being slowly formed.

Figs. 5 and 6 show the R_F -concentration and R_M -log concentration relationships for HSbCl_6 developed with H_2SO_4 or H_3PO_4 . In H_2SO_4 the hydrolysis is quite considerable; however, the HSbCl_6 spot is always clearly distinguishable. The change of the R_F values follows closely that observed with HAuCl_4 . In dilute (less than 1 N) acids the results with HSbCl_6 in conc. HCl are not highly accurate as the conc. HCl influences the movement of the spot of the Sb(V) solution over quite a distance.

For the data with solutions more concentrated than 1 N (with respect to H_2SO_4 or H_3PO_4) there seems to be a 1:1 slope for the R_M -log concentration relation for H_3PO_4 and a 1:2 slope for H_2SO_4 . Thus essentially the same effects are obtained as with HAuCl_4 and HAuBr_4 .

SUMMARY

The solution chemistry of SbCl_5 in aqueous HCl , H_2SO_4 and H_3PO_4 was studied by adsorption chromatography on cellulose, partition chromatography and ion exchange.

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