Inorganica Chimica Acta, 28 (1978) L155–L156
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Structure in Solution and Acetonitrile Intermolecular Exchange Process of the Antimony Pentachloride–Acetonitrile Adduct

RENÉ GOOD, DONALD R. ZBINDEN, J. ETIENNE KESSLER AND ANDRÉ E. MERBACH*

Institut de chimie minérale et analytique, Université de Lausanne, 3, Place du Château, CH-1005 Lausanne, Switzerland

Received March 30, 1978

As a result of our continuing interest in mechanisms of ligand substitution reactions at octahedral metal complexes [1], we explored the structure and ligand-exchange patterns of the $SbCl_5 \cdot CH_3CN$ adduct, applying IR, Raman, ^{13}C-NMR, ^{121}Sb-NMR and ^1H-NMR techniques. The exchange itself

$$SbCl_5 \cdot CH_3CN + CH_3CN^* \rightleftharpoons SbCl_5 \cdot CH_3CN^* + CH_3CN \qquad (1)$$

has been studied by ^1H-NMR, yielding a first-order rate-law along with activation parameters ΔH^* of 68 ± 3 kJ mol^{-1} and ΔS^* of $+82 \pm 14$ J K^{-1} mol^{-1} in support of a dissociative D mechanism for the ligand exchange reaction.

The long-known ability of antimony pentachloride to form, among other things, 1:1 adducts with electron-donating agents [2] was emphasized by Gutman using it as a reference acid for his donor strength scale. Further reports in the literature [3], together with our experience of transition metal halides convinced us that the situation with 1:1 adducts is not always straightforward and demands close scrutiny. Particularly, we felt it necessary to back up a kinetic investigation by an assessment of the species that can be found in a dilute solution of $SbCl_5$ and acetonitrile in dichloromethane. The Raman spectrum in the region where metal–chlorine vibrations are found conforms to the pattern expected for a C_{4v} point group, supporting an octahedral structure for $SbCl_5 \cdot CH_3CN$, in agreement with previous studies conducted under different experimental conditions [4]. The often observed or postulated [3] presence of ionic species of the type $SbCl_6^-$ and $SbCl_4^+$ or $SbCl_4 \cdot 2L^+$ where L is an electron-donating species demanded a second preliminary investigation. Raman spectroscopy was used again since the spectrum of the totally symmetric $SbCl_6^-$ species pertaining to the O_h point group is well-known and quite different from the one characterizing the adduct. By using solvents of increasing polarity (dichloromethane and varying amounts of nitromethane) one would expect a progressive replacement of the adduct spectrum by that of $SbCl_6^-$ and such is indeed the case. Furthermore, preliminary results seem to indicate that ionization is directly dependent upon two factors. Firstly, the polarity of the solvent and secondly, the donor strength of the ligand. Some caution ought to be exerted though, in the choice of a polar solvent. A case in point is nitromethane *vs.* nitrobenzene. A ^1H-NMR study of an $SbCl_5$–HMPA (hexamethylphosphoramide) adduct in nitrobenzene [5] leads to the conclusion that the solution contains slow-exchanging $SbCl_5 \cdot HMPA$, fast-exchanging $SbCl_4 \cdot 2HMPA^+$ and free HMPA. An attempt to duplicate this experiment in nitromethane failed, although the dielectric constant of both solvents is practically the same. Only one signal was observed, indicating a fast exchange between the species present in solution. An explanation of this behaviour could be found by taking a ^{13}C-NMR spectrum of a solution of nitrobenzene in dichloromethane and then adding an equivalent amount of $SbCl_5$. Upon this operation, the resonance of the para-carbon is shifted downfield by 1.9 ppm, suggesting a definite interaction between the solutes. One can therefore envision a stabilization of the $SbCl_5 \cdot HMPA$ adduct via a ternary complex with nitrobenzene, while such an effect is negligible in nitromethane.

As mentioned already, the Raman spectrum of $SbCl_6^-$ differs significantly from that of $SbCl_5 \cdot CH_3CN$. However, the position of the bands for the two species is such that the detection of small amounts of ionized $SbCl_5$ next to the adduct is prevented. Since the ligand-exchange rate for complexes of the type $SbCl_4 \cdot 2L^+$ might influence profoundly the exchange phenomena on the adduct, a study of charged compounds of this type has been started in our laboratory. In the meantime, we focused our attention on systems in which the amount of dissociation is believed to be negligible. As we were still in need of a technique allowing us to prove this last point, we made use of ^{121}Sb-NMR. While the results were disappointing for $SbCl_5 \cdot L$, $SbCl_4^+$ and $SbCl_4 \cdot 2L^+$ owing to the line-broadening caused by the quadrupole moment of ^{121}Sb allied to an environment of relatively low symmetry, they were most encouraging for $SbCl_6^-$. Successive dilutions showed that this highly symmetric ion can be detected easily to a concentration lower than 10^{-3} *M*. This technique was used to assess the absence of ionization in dilute solutions of antimony pentachloride and acetonitrile in dichloromethane, thus enabling a straightforward kinetic study on the adduct. Solutions were prepared in a dry box by mixing 99.99% $SbCl_5$ with acetonitrile in dichloromethane, the latter two being dried over phosphorus pentoxide, distilled and stored over

---

*Address all correspondence to this author.

4 Å molecular sieves. A typical solution was 0.05 *m* in $SbCl_5$ and 0.10 in CH_3CN. Vibrational equipment included a Perkin-Elmer 577 IR spectrophotometer and a Spex CompAct Raman Spectrometer. NMR spectra were recorded on a Bruker WP-60 Fourier Transform spectrometer. The 1:1.00 ± 0.03 stoichiometry of the adduct was established in solution by integrating the signal due to the complex with respect to the signal arising from the ^1H-^{13}C coupling in the solvent. The solutions contained to TMS, since chlorination by $SbCl_5$ occurs readily. The working reference was dichloromethane, but for the sake of clarity, results are given with respect to TMS, assuming $\delta_{CH_2Cl_2}$ to be 5.32 ppm. The line-shapes of the free and bound acetonitrile in the ^1H-NMR spectra were analyzed with the EXCHNG program [6].

The results fall into four parts: 1) The investigations mentioned above demonstrate that eq. (1) is an adequate description of the exchange reaction in the type of solutions considered in this study. 2) The single ^1H-resonance of complexed acetonitrile at 283 K, where the exchange process is immeasurably slow, is located at 2.64 ± 0.01 ppm with respect to TMS. Under these conditions, the resonance of free acetonitrile is found at 1.98 ± 0.01 ppm. 3) In a constant-temperature experiment, the ligand exchange rate was found to be independent of the concentration in free ligand over a ten-fold range. The resulting rate law is

$$\frac{d[SbCl_5\cdot CH_3CN]}{dt} = k_1[SbCl_5\cdot CH_3CN] \qquad (2)$$

characteristic of a first-order reaction. 4) Seventeen measurements at temperatures ranging from 214 to 255 K were interpreted with a linear least-squares fitting program (correlation coeff. 0.992). The activation enthalpy has thus been found to be 68 ± 3 kJ mol^{-1} and the activation entropy 82 ± 14 J K^{-1} mol^{-1}.

For d^0 systems such as $NbX_5\cdot L$ or $TaX_5\cdot L$ (X = Cl, Br), the substitution has been shown to change from D to I_a when soft donor atoms are involved [7]. We think it worthwhile to find out if a d^{10} central atom as antimony (V) in the pentachloride, can react via an I_a mechanism. At present, the first findings mentioned above support a D mechanism in the case of acetonitrile. We hope to attain broader conclusions by examining a variety of ligands and by volume of activation measurements as can be achieved through high pressure nuclear magnetic resonance [8].

Acknowledgments

We wish to thank Dr. William L. Earl for taking the ^{121}Sb-NMR spectra and the Swiss National Science Foundation for financial support under Grant 2.675-0.76.

References

1 a) R. Good and A. E. Merbach, *Inorg. Chem.*, *14*, 1030 (1975).
b) C. M. P. Favez and A. E. Merbach, *Helv. Chim. Acta*, *60*, 2695 (1977).
c) S. J. Ruzicka, C. M. P. Favez and A. E. Merbach, *Inorg. Chim. Acta*, *23*, 239 (1977).
2 M. Webster, *Chem. Rev.*, *66*, 87 (1966).
3 a) I. Y. Ahmed and C. D. Schmulbach, *Inorg. Chem.*, *11*, 228 (1972).
b) P. Stilbs and G. Olofsson, *Acta Chem. Scand.*, *A28*, 647 (1974).
4 a) D. M. Byler and D. F. Shriver, *Inorg. Chem.*, *13*, 2697 (1974).
b) M. Masson, Z. A. Payne, M. J. F. Leroy, *Spectrochim. Acta*, *33A*, 37 (1977).
5 See ref. [3] b).
6 See details and references in ref. [1] b).
7 Described in ref. [1] a).
8 For example in A. E. Merbach and H. Vanni, *Helv. Chim. Acta*, *60*, 1124 (1977).