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Received December 4, 1958.

## On the Relative Donor Strengths of $\text{POCl}_3$ and $\text{PO}(\text{CH}_3)_3$ .

### A Ramanspectroscopic Study

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A very important problem in the study of addition compounds is the determination of the relative acceptor and donor strengths of the reacting molecules.

The relative donor strengths of two donor molecules  $D_1$  and  $D_2$  are only defined for a given acceptor molecule  $A$ . The free energy changes of the two reactions  $A(\text{g}) + D_1(\text{g}) = AD_1(\text{g})$  and  $A(\text{g}) + D_2(\text{g}) = AD_2(\text{g})$  should be compared in an exact study. If liquid or solid phases appear in either of these reactions the discussion is complicated by the large variations in cohesive energies. These depend very much upon the dipole moments of the different molecules, and bear no obvious relation to the strengths of the acceptor-donor bonds. The same difficulty prevails if a solvent with an appreciable dipole moment is used for the study. In an ideal solvent the differences between the solvation energies for  $D_1$  and  $AD_1$ , and for  $D_2$  and  $AD_2$  should be equal. It is rather difficult to find such a solvent but the use of different types of solvents which may interact more or less

favourably with the different molecules might lead to a rather safe assessment of the relative donor strengths.

If such solvents can be selected a suitable method of studying the reactions taking place remains to be found so that at least the order of donor strength can be determined. The molecular spectra are then of an especial interest although they do not seem to have been used much for this purpose. Infrared spectra and Raman spectra each have their advantages and disadvantages in this connection. IR is sensitive to low concentrations of the dissolved molecules if the solvent has a low absorption in the spectral regions where the molecules to be studied absorb. Raman spectra are more difficult to measure in dilute solutions but have fewer absorption bands with less risk for overlap between the spectra of the different molecules or with the solvent spectrum. In this first study we have investigated the usefulness of the Raman method.

For this purpose we have tried to find a test pair of donor molecules with well known donor functions for which a rather safe prediction about the relative donor strengths could be made, so that the difficult search for a number of different, suitable solvents could be omitted as an unnecessary precaution. This requirement is fulfilled by the pair  $\text{POCl}_3$  and  $\text{PO}(\text{CH}_3)_3$ . The donor function of the oxygen atom in such compounds has recently been definitely established by X-ray and spectroscopic work<sup>1,2</sup>. It can also be safely predicted that  $\text{PO}(\text{CH}_3)_3$  should be a better donor molecule than  $\text{POCl}_3$ . The larger electronegativity of chlorine causes a drift of electrons from oxygen in  $\text{POCl}_3$  compared with  $\text{PO}(\text{CH}_3)_3$  and thus a lower dipole moment and a lower tendency to donate an electron pair.

1,2-Dichlorethane was used as a solvent and the following solutions were studied (mole fractions within brackets):  $\text{POCl}_3$  (0.10),  $\text{PO}(\text{CH}_3)_3$  (0.10),  $\text{SbCl}_5 + \text{POCl}_3$  (0.10 + 0.10),  $\text{SbCl}_5 + \text{PO}(\text{CH}_3)_3$  (0.02 + 0.02) and  $\text{SbCl}_5 + \text{POCl}_3 + \text{PO}(\text{CH}_3)_3$  (0.02 + 0.02 + 0.02). The solution of  $\text{SbCl}_5 \cdot \text{POCl}_3$  was supersaturated. The preparation of the mixture of all three molecular species must be made in such an order that  $\text{POCl}_3$  and  $\text{PO}(\text{CH}_3)_3$  are not permitted to react with each other. The products of that complicating reaction are not known but the reaction is prevented by the presence of  $\text{SbCl}_5$ .

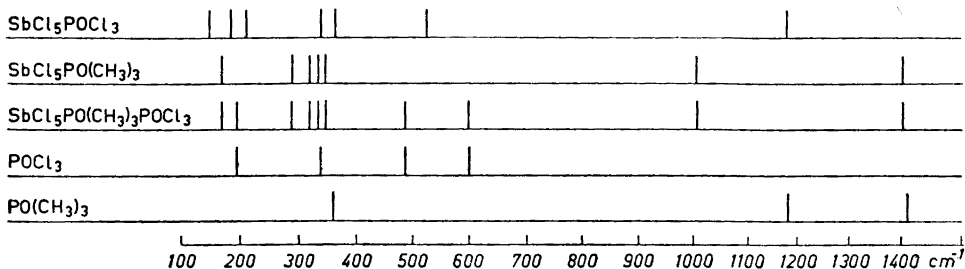


Fig. 1. The Raman spectra of the different solutions.

The Raman spectra were taken with a redesigned spectrograph of the type described by Kinell<sup>3</sup>. The photographic technique using Ilford Zenith plates was applied. The spectra were excited by the 4358 Å Hg-line, and saturated NaNO<sub>2</sub> solution was used to filter away the UV part of the Hg-spectrum.

The results are shown in the simplified Fig. 1 where the spectrum of 1,2-dichloroethane is omitted together with those bands which overlap with it (the intensities are not indicated).

The interpretation is obvious: all the SbCl<sub>5</sub> in the ternary mixture has reacted with PO(CH<sub>3</sub>)<sub>3</sub> to form SbCl<sub>5</sub> · PO(CH<sub>3</sub>)<sub>3</sub>, leaving POCl<sub>3</sub> unreacted in the solution. This confirms that PO(CH<sub>3</sub>)<sub>3</sub> is a better donor molecule than POCl<sub>3</sub> in the reaction with SbCl<sub>5</sub> (at these concentrations in 1,2-dichloroethane, strictly speaking).

The very distinct determination of the relative donor strengths achieved by this method in this case gives good hope for its application to problems with a less obvious solution. Such work is in progress in these Institutes.

A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

Finally we wish to thank Professor S. Claesson and Professor G. Hägg for all facilities put at our disposal.

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Received December 11, 1958.

## Corrections to "A Group Separation Method for Gamma Spectrometry of Complex Radionuclide Mixtures"\*

K S A M S A H L \*\*

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P. 1293, line 11 from below,

*for*

Besides its powerful solving and oxidizing action on many elements it will for example reduce possible higher valences of manganese to the divalent state and does not effect oxidation of trivalent chromium in hydrochloric acid. As a result chromium, if not initially present as chromate, and manganese can easily be quantitatively separated from other elements.

*read*

Besides its powerful, solving and oxidizing action on many elements it will for example reduce possible higher valences of manganese to the divalent state and chromates to trivalent chromium in hydrochloric acid. As a result chromium and manganese can easily be quantitatively separated from other elements.

\* *Acta Chem. Scand.* **12** (1958) 1292.

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Received December 20, 1958.