$$\mathrm{PyH^+ + Pic^-} \overset{K_a}{\rightleftharpoons} \mathrm{PyHPic}, K_a = \frac{[\mathrm{PyHPic}]}{[\mathrm{PyH^+}]\,[\mathrm{Pic^-}]\,f_\pm^2}$$

(*3*) the homoconjugation constant K_1^+

$$\mathrm{PyH^+ + Py} \overset{K_1^+}{\rightleftharpoons} \mathrm{(PyHPy)^+}, K_1^+ = \frac{[\mathrm{PyHPy^+}]}{[\mathrm{PyH^+}]\,[\mathrm{Py}]}$$

In addition to these, the formation of 1:2 complexes between the pyridinium ion and the pyridine molecule is observed in the case of 3,4-dimethylpyridine and 4-dimethylamino pyridine. This may be explained in terms of π–π interactions between the second pyridine molecule and that already bound to the cation by a hydrogen bond.

Plots of $\log K_f$, $\log K_a$ and $\log K_1^+$ *vs.* aqueous pK_a s values of the pyridines yield straight lines with slope of 1.167, −0.218 and 0.061 respectively. The results show that the hydrogen bond formation between pyridine and picric acid in nitrobenzene increases with increasing basicity of the pyridine molecule. The value of the first slope indicates that the proton transfer is important. The ionic association between the pyridinium cation and the picrate anion increases with increasing acidity of the cation. In the case of the formation of the homoconjugate cation $\mathrm{PyH^+\cdots Py}$ it was expected that the substituent effects will be small, because the increasing proton donor ability of the cation will be compensated by the decreasing proton acceptor ability of the conjugate base. It is interesting to note that, contrary to this expectation, the stability of the non-*ortho* substituted homoconjugate cation increases, although to a small extent, with the basicity of the pyridine. This is explained by considering the potential energy curve of the proton for the homoconjugate cation. The increase of the depth of the potential well resulting from the hydrogen bond formation is more important when the pyridine is more basic.

A Study of the Solvent Effect on the Raman Parameters of Halogen and Interhalogen Vibration Bands

G. MAES†

University of Leuven, Department of Chemistry, Celestijnenlaan 200F, 3030 Heverlee, Belgium

The $\nu_{\mathrm{Br-Br}}$ Raman band of bromine dissolved in several solvents was studied. The observed frequency shifts relative to the gas phase value were correlated with the Krikwood–Bauer–Magat function:

$$\frac{\Delta\nu}{\nu} = C\,\frac{\epsilon - 1}{2\epsilon + 1}$$

Important deviations were observed for the solvents which are known to form specific charge transfer complexes with bromine, and also for CS_2.

The absolute intensity of the bromine Raman vibration band was calculated from relative intensity measurements. Also the depolarization degree ρ was measured. These measurements allowed to calculate the polarizability derivatives $(\alpha'_R)_\parallel$ and $(\alpha'_R)_\perp$.

The ρ factor increases when the polarity of the solvent increases or when specific interactions bromine–solvent occur. Two different relations for the inert solvents and for the interacting solvents were observed on comparing ρ with $\Delta\nu/\nu$. This must be explained by the increase of the parallel polarizability component $(\alpha'_R)_\parallel$ as a result of the specific interaction with the solvent.

The half band width of the bromine band was found to be smaller than the corresponding infrared band and this is explained by the fact that the Raman band is only partially polarized. The relation between the increase of the half band width and the ρ value supports this explanation.

The results for the $\nu_{\mathrm{Br-Br}}$ band are compared with those of a new study on the $\nu_{\mathrm{I-Br}}$ band parameters in these solvents.

---

†Aangesteld Navorser' of the Belgian N.F.W.O.

Specific Interactions of Trifluoroacetate Ion and Trifluoroacetic Acid in Nitrobenzene

Z. PAWELKA

Institute of Chemistry, University 50 383 Wrocław, Poland

and M. Cl. HAULAIT-PIRSON

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, 303 Heverlee, Belgium

The conductances of solutions of triethylammonium trifluoroacetate ($Et_3NHCOOCF_3$) in nitrobenzene have been measured in order to study the ionic association:

$$\mathrm{Et_3NH^+ + CF_3COO^-} \overset{K_A}{\rightleftharpoons} \mathrm{Et_3NH^+\cdots{}^-OOCCF_3}$$

Using the Fuoss linear relationship [1] for solutions covering the concentration range 10^{-4}–10^{-3} *M*, the association constant K_A has been evaluated ($K_A = 3\cdot10^5$ dm^3 mol^{-1}). This constant is two orders of magnitude greater than that observed for triethylammonium picrate in the same solvent [2] (HPic and CF_3COOH have the same aqueous pK_a's values). For salt concentrations ranging from 10^{-3} to 5.10^{-3} *M*