An Infrared-spectroscopic Study of Adduct Formation between Bis(acetylacetonato)oxovanadium(IV) and Substituted Pyridines

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Summary Infrared-spectral measurements of adduct formation between VO acac$_2$ (Hacac = pentane-2,4-dione) and a range of substituted pyridines provide evidence for an equilibrium between geometrical isomers in chloroform solution.

ONE of the most useful probes for the study of adduct formation between VO acac$_2$ and Lewis bases has been the effect of the additional co-ordination on the fundamental stretching frequency of the V=O bond (ν_{VO}).[1] Recently, Garvey and Ragsdale[2] found good correlation between the magnitude of the shift of this i.r. band and a calculated Hammett σ' factor for a series of substituted pyridine *N*-oxide adducts in solution. We report here a similar study of the i.r. spectra of substituted pyridine adducts, but with very different results.

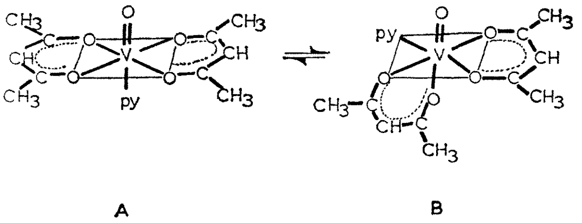
The spectra were recorded for chloroform solutions of the pyridine and VO acac$_2$ in an approximately 5 : 1 molar ratio. In all cases the ν_{VO} of VO acac$_2$ at 1003 cm.$^{-1}$ was considerably diminished in intensity and corresponding, well defined adduct bands were easily identified. The results, together with the relevant Hammett σ' factors,[3] are presented in the Table. Instead of the expected correlation of the shift of ν_{VO} with σ', approximately fixed shifts of 31 $\mp$ 3 cm.$^{-1}$ and/or 51 $\mp$ 3 cm.$^{-1}$ are observed in all cases. The more basic pyridines give only the ν_{VO} of larger shift, but, as the basicity of the pyridines decreases, this band falls in intensity and the ν_{VO} of smaller shift becomes predominant, until for 3-cyanopyridine the former band is completely absent. 2-Methylpyridine, the only 2-substituted pyridine studied, is slightly anomalous in that it gives both shifted bands of approximately equal intensity, despite its low σ' value. Experiments with varying ratios of the pyridine to VO acac$_2$ (1 : 1, 2 : 1, 5 : 1, and 10 : 1) or with the addition of an excess of Hacac showed that the intensity ratio of the two bands, for the cases where they are observed, is independent of the concentration of the ligands.

TABLE

Substituent	σ'	ν_{VO} bands (cm.$^{-1}$) and relative intensity	
3-CN	+0·64		975
4-CN	+0·55	951	$<$ 975
3-Cl	+0·40	955	$\sim$ 972
3-Br	+0·39	955	$\sim$ 974
3-CHO	+0·26	953	$>$ 972
4-Br	+0·24	953	$>$ 969
4-Cl	+0·23	953	$>$ 969
4-CHO	+0·11	953	$\gg$ 971
3-OH	+0·07	950	
H	0	955	
3-Me	−0·08	953	
4-Me	−0·14	954	$\gg$ 971
3-NH$_2$	−0·14	952	
4-NH$_2$	−0·65	949	
2-Me	−0·13	954	$\sim$ 975

The occurrence of fixed shifts for the ν_{VO} of VO acac$_2$ on further co-ordination has been noted before for adducts with a variety of Lewis bases, but no explanation of this phenomenon was offered.[1] The present observation of two shifted bands for some of the substituted pyridine adducts provides evidence for the existence of an equilibrium between two distinct types of complex in solution.

The independence of this equilibrium of the ligand concentrations for a particular pyridine further suggests that these complexes are isomers, and, most likely, the complexes (A) and (B). The *trans*-co-ordination of the pyridine with respect to the V=O bond in isomer (A) would be expected to have a larger effect on ν_{VO} than the *cis*-co-ordination of isomer (B). A *cis*-arrangement of the chelate rings as in (B) is not unlikely, and has been demonstrated for the complex Ni acac$_2$ (pyridine *N*-oxide)$_2$ and some cobalt(II) complexes of acac.[4]



FIGURE

The effect of the basicity of the pyridine on the position of equilibrium may be explained as a competition between ligand strength and steric effects; the angle of 106° between axial and equatorial oxygen atoms in VO acac$_2$[5] indicates that a certain amount of steric hindrance would be met by a ligand approaching *trans* to the V=O bond, and *trans*-adduct formation would therefore be expected only for the more strongly co-ordinating ligands. In (B), steric effects are smaller so co-ordination is open to the weaker ligands to form this presumably thermodynamically less favoured isomer. This reasoning accounts for the case of 2-methylpyridine which, by virtue of its greater effective bulk, would favour isomer (B) more than usually. It remains, however, difficult to understand the fixed amounts of both shifts, rather than a trend in their values with σ', but it is not inconceivable that this may again reflect an interplay of both steric and inductive effects.

Attempts are in progress to isolate isomers of types (A) and (B) in the solid state in order to establish the foregoing interpretation firmly. Preliminary results in the solid state have shown that only one ν_{VO} is observed in all the isolated adducts and the shift of ν_{VO} occurs over a range of values. In some cases this gives rise to large differences between the ν_{VO} values for solution and solid.

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