

THE PROTON MAGNETIC RESONANCE
CONTACT SHIFT STUDIES ON COBALT(II)
HALIDE COMPLEXES OF PYRIDINE N-OXIDE
AND DIPHENYL SULPHOXIDE

Introduction

THIS investigation is carried out to arrive at the anion effect on the metal-neutral ligand bonding. In order to discuss these effects, the spin-delocalisation mechanisms that give rise to pmr contact shifts and the effects of halide anions on the cobalt-neutral ligand bonding must be considered. It has already been reported that the composition and configuration of Co(II) halide complexes of pyridine N-Oxide (PNO) and diphenyl sulphoxide (DPSO) vary depending on the nature of the halide anion¹⁻⁶. But very limited number of contact shift studies on cobalt(II) halide complexes with these ligands is reported⁷⁻⁹. Moreover, it will be interesting to know how the contact shift studies can be made use of, to predict the effect of the halide anions on the bonding of the metal to the various neutral monodentate ligands.

Experimental

Cobalt(II) halides and perchlorate complexes of (PNO) and (DPSO) were prepared by methods reported previously¹⁻⁶. Their configurations were assigned from their conductance, magnetic susceptibility, infrared and electronic spectral data. PMR contact shift measurements were made in 60 MHz Varian NMR spectrophotometer with 0.1 M solutions of the complexes containing a slight excess of the neutral ligand in CD₃CN. The results are given in Table I. The proton resonance shifts (Table I) are shifts in the resonance frequencies from their normal values in the absence of the paramagnetic complexes measured in cps with an error of ± 0.5 cps. Negative shifts indicate shifts to lower applied field.

Results and Discussion

In general, the delocalisation mechanism can be understood if we consider the main effects which can contribute to the observed pmr shifts of the octahedral cobalt(II) complexes. Cobalt(II) has three unpaired electrons, two e_g and one t_{2g} electrons. The e_g electrons are responsible for the mechanism of σ -spin delocalisation. The t_{2g} electrons can be transferred on to ligands only in the case when π -bonds are formed between the metal ion and the ligands (π -delocalisation). The π -delocalisation is significant for planar ligands and usually dominate when it is present in the Co(II) complexes.

However, six-coordinated Co(II) complexes have a triply degenerate ground state which is expected to produce magnetic anisotropy and hence significant pseudo-contact shift. This is particularly important in the case of distorted DPSO complexes. Even in the case of PNO complexes (O_h) substitution by the solvent can introduce significant pseudo-contact contribution even in the presence of rapid exchange.

According to Wayland and Drago⁹, the relative amount of metal-neutral ligand covalent bonding depends upon the energy the metal halide acceptor valence orbitals. Application of their molecular orbital bonding model leads to the prediction that the energy (destabilisation) of the MX_2 acceptor orbitals increases in the order $MCl_2 > MBr_2 > MI_2$. The magnitude of the metal-neutral ligand covalent bonding is thus expected to increase in the order $MCl_2 \cdot xL < MBr_2 \cdot xL < MI_2 \cdot xL$. This will be the case only if there is an increase in ligand proton contact shifts when the anion is changed from Cl^- to Br^- or I^- . The coordinated anion may impart greater contact shifts than the uncoordinated anion. Accordingly the observed shifts are expected to be in the

TABLE I

PMR shifts in ligand protons in Co(II) halide and perchlorate complexes with PNO and PDSO

Complexes	Stereo Chemistry	Δv_α	Δv_β	Δv_γ
1. $[Co(PNO)_6]^{2+} [CoCl_4]^{2-}$	Octahedral cation with tetrahedral anion	+ 14	+ 2	+ 2
2. $[Co(PNO)_6] (ClO_4)_2$	Octahedral	+ 20	- 4	+ 24
3. $[Co(PNO)_6] I_2$	Octahedral	+ 16	- 6	+ 22
4. $[Co(PNO)_4 Br_2]$	Distorted octahedral	+ 18	+ 24	+144
5. $[Co(DPSO)_2 Cl_2]$	Distorted tetrahedral	+ 6	+ 58	+ 18
6. $[Co(DPSO)_4 I_2]$	Distorted octahedral	- 66	- 30	- 8
7. $[Co(DPSO)_6] (ClO_4)_2$	Octahedral	-166	- 78	- 40
8. $[Co(DPSO)_6]^{2+} [CoBr_4]^{2-}$	Octahedral cation with tetrahedral anion	- 93	-43	- 7

order $\text{Cl}^- > \text{Br}^- > \text{I}^- > (\text{CoBr}_4)^{2-} > (\text{CoCl}_4)^{2-} > \text{ClO}_4^{2-} > \text{I}^-$ (uncoordinated).

However in the present investigation, such a regular increase in contact shifts is not observed. This is due to the fact that as the anion is changed, the configuration of the complexes changes from octahedral to either distorted octahedral or pseudo-tetrahedral. Distortion in regular geometry leads to magnetic anisotropy which is responsible for the dipolar effects. Separation of the observed averaged out shifts for these complexes, into contact and dipolar contributions, is necessary in order to explain the variations in covalency of the metal-neutral ligand bonding. Unless absolute shifts can be observed or calculated, it is difficult to detect the effect of co-ordinated anions on the neutral ligand. Further work is in progress on this line of investigation.

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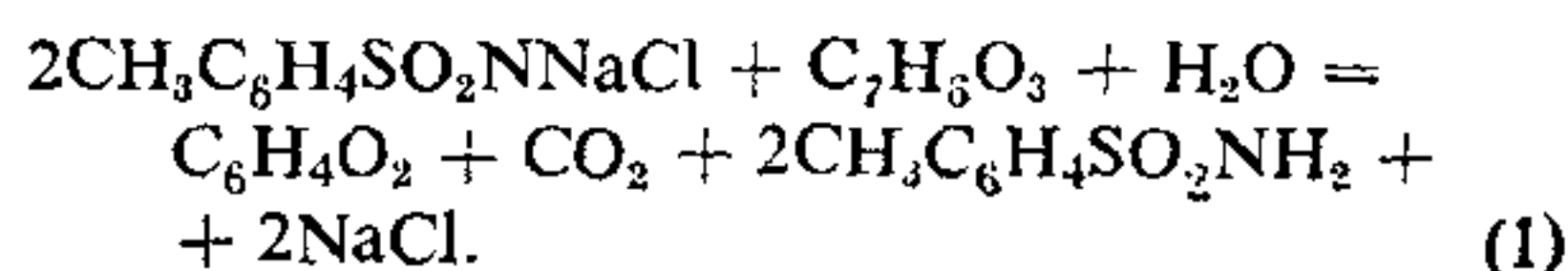
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KINETICS AND MECHANISM OF OXIDATION OF SOME SUBSTITUTED BENZOIC ACIDS BY CHLORAMINE-T IN ALKALINE MEDIA

CHLORAMINE-T (CAT), the sodium salt of *p*-toluene sulphochloramide, is a powerful oxidising agent and has been widely used for the oxidation and estimation of several organic and inorganic compounds¹⁻⁴. Generally it undergoes a two electron change per mole in all these oxidations⁵. In the present work, the chloraminometric oxidations of *p*-hydroxybenzoic acid (I), *m*-hydroxybenzoic acid (II) and *O*-hydroxybenzoic acid (III) have been studied. Some work on the peroxydisulphate oxidation kinetics of the above compounds has already been reported.

Experimental

The solutions of the substrates were prepared in 50% methanol from AnalaR B.D.H. samples. The experimental procedures have been described in our earlier paper⁷. Experiments showed that one mole of substrate consumed two moles of CAT according to the following stoichiometric equation:



The product *o*-benzoquinone was identified by conventional spot test method⁸.

Results and Discussion

The kinetic investigations were carried out at several initial concentrations of the reactants at constant $[\text{OH}^-]$. The disappearance of CAT obeys first order kinetics and the pseudo first order rate constants k_1' calculated are given in Table I. The pseudo first

TABLE I

Effect of reactants' concentrations on the reaction rate
 $[\text{NaOH}] = 2.0 \times 10^{-2} \text{ M}$

10 ³ M [CAT]	10 ² M [substrate]	$k_1' \times 10^3 \text{ sec}^{-1}$					
		I		II		III	
		45'	50'	45'	50'	45'	50'
0.8	1.8	4.7	5.6	4.2	5.0	3.6	4.2
1.0	1.8	4.7	5.5	4.1	5.0	3.6	4.2
1.2	1.8	4.7	5.5	4.2	5.1	3.5	4.2
1.6	1.8	4.6	5.6	4.2	5.0	3.7	4.2
2.0	1.8	4.7	5.6	4.2	5.1	3.6	4.2
1.0	1.2	3.2	3.9	3.0	3.3	2.4	2.8
1.0	1.4	3.8	4.3	3.4	3.4	3.0	3.2
1.0	2.2	6.2	7.5	5.2	6.0	4.5	5.1
1.0	2.6	8.9	10.4	7.0	7.8	5.8	6.4