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Calculation of CO Stretching and Interaction Force Constants for Mono(tetracarbonylcobalt) Derivatives of Tin(IV) Based on the Approximation of Paul

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CO stretching and interaction force constants have been calculated for mono(tetracarbonylcobalt) compounds of tin(IV) and for some of their phosphine substituted derivatives. It is shown that the CO bond order reflects the changing nature of the cobalt–tin σ-bond.

Introduction

The force constants (k_a, k_e, c' and c) are calculated for some 25 carbonyl compounds containing a Sn–Co bond. k_a and k_e refer to the stretching force constants of the axial and equatorial CO groups, c' and c are the CO_{eq}–CO_{eq} and CO_{eq}–CO_{ax} interaction constants. The secular equations in a modified Urey–Bradley force field for the CO vibrations in $LCo(CO)_4$ species are given in the literature [1]. There are four force constants which must be evaluated from three vibration frequencies. Therefore the calculations will be done using the approximation of Paul, *et al.* [2]. A value of c'/c corresponding to maximum allowable coupling between both A_1 modes will be derived directly from the observed carbonyl frequencies:

$$(c'/c)_{max} = (X + Y - 2Z)/\sqrt{3}(X - Y),$$

X, Y and Z are the λ/μ values calculated from the $A_1(1)$, $A_1(2)$ and E stretching frequencies, respectively. This leads to values of c'/c of about 1.1.

Other considerations may lead to other ratios of c'/c. So Darensbourg and co-workers [3, 4] have shown that the c'/c ratio giving the best agreements with the isotopic ^{13}CO bands lies around 1.4. If instead of using $(c'/c)_{max}$, c'/c = 1.4 is used, the numerical values of the force constants will of course be changed. However, as shown in Table I for $(CH_3)_3SnCo(CO)_4$ and $Cl_3SnCo(CO)_4$, the general trends revealed in our discussion will hold.

The force constants for the phosphine substituted tricarbonylcobalt tin(IV) derivatives can be obtained directly from their secular equations (two equations, two force constants).

Results and Discussion

Regarding the data given in Table I two interesting features have to be noticed. First it is found that for all the compounds under study k_a exceeds k_e. Second, in going from the fully methylated to the fully halogenated derivatives the two stretching force constants steadily converge. The first observation is in accord with symmetry considerations. In a trigonal bipyramidal $LCo(CO)_4$ derivative the transition metal has two sets of *d* orbitals, $d_{x^2-y^2}$, d_{xy}(E) and d_{xz}, d_{yz}(E), which can be seen as essentially available for π-bonding. Since the equatorial CO groups may interact with both these sets, the [Co–C] O π-bond order will be the greatest for the equatorial groups and consequently k_e will be lower than k_a. As a corollary to this, it is obvious that within the series R_{3-n} $X_nSnCo(CO)_4$ the equatorial force constant is more variable than the axial one. A σ-electron withdrawing group, such as a halogen substituted tin ligand, will tend to contract the transition metal *d* orbitals, thereby reducing the over-all metal to carbon monoxide π-bonding. Nevertheless since the axial CO group can only π bond with two *d* orbitals (d_{xz}, d_{yz}) this effect has a greater influence upon k_e than upon k_a. Therefore the two force constants will converge in going from n = 0 to n = 3, as is observed. The above discussion implies that the effect of the halogens bound to the tin metal is transmitted to the transition metal by a purely inductive mechanism through a very polarisable σ metal–metal bond.

In an attempt to confirm this proposition plots of CO stretching force constants against quantities measuring the inductive electron-withdrawing capacity of the tin substituents have been drawn. A good result is obtained by plotting the force constants against the Taft σ*values of XCH_2 groups [5]. The correlations are shown in the Figure. It is clearly seen that the points lie on two straight lines, all the methyl derivatives falling on the upper line, the phenyl substituted derivatives on the lower one. So the effective electronegativity of a phenyl group seems to be less than expected from its σ* value. This we explain by assuming an interaction between the π-

TABLE I. Approximate Valence and Interaction Force Constants Assuming Maximum Allowable Coupling between Both the A_1 Modes (mdynes/Å).

	Compound	k_a	k_e	c'	c	$(c'/c)_{max}$	$\Delta k_{a,e}$
(1)	$(CH_3)_3SnCo(CO)_4$[a]	16.99	16.30	0.343	0.296	1.160	0.69
		16.83	16.35	0.395	0.282	(1.4)	0.48
(2)	$(C_2H_5)_3SnCo(CO)_4$[b]	16.94	16.25	0.343	0.305	1.124	0.69
(3)	$(C_6H_5)_3SnCo(CO)_4$[a]	17.09	16.45	0.318	0.288	1.105	0.64
(4)	$(CH_3)_2ClSnCo(CO)_4$[c]	17.24	16.57	0.333	0.279	1.191	0.67
(5)	$(C_4H_9)_2ClSnCo(CO)_4$[e]	17.17	16.51	0.332	0.279	1.191	0.66
(6)	$(C_6H_5)_2ClSnCo(CO)_4$[c]	17.28	16.65	0.314	0.275	1.143	0.63
(7)	$(CH_3)_2BrSnCo(CO)_4$	17.22	16.57	0.327	0.279	1.171	0.65
(8)	$(C_6H_5)_2BrSnCo(CO)_4$[c]	17.27	16.65	0.311	0.270	1.153	0.62
(9)	$(CH_3)_2ISnCo(CO)_4$	17.21	16.55	0.327	0.279	1.172	0.66
(10)	$(C_6H_5)_2ISnCo(CO)_4$[c]	17.24	16.62	0.308	0.270	1.143	0.62
(11)	$CH_3Cl_2SnCo(CO)_4$	17.48	16.86	0.310	0.257	1.207	0.62
(12)	$C_4H_9Cl_2SnCo(CO)_4$[c]	17.46	16.85	0.305	0.262	1.164	0.61
(13)	$C_6H_5Cl_2SnCo(CO)_4$[c]	17.49	16.89	0.300	0.262	1.144	0.60
(14)	$CH_3Br_2SnCo(CO)_4$	17.45	16.84	0.305	0.257	1.186	0.61
(15)	$C_6H_5Br_2SnCo(CO)_4$[c]	17.46	16.87	0.294	0.262	1.123	0.59
(16)	$CH_3I_2SnCo(CO)_4$	17.38	16.78	0.301	0.256	1.175	0.60
(17)	$C_6H_5I_2SnCo(CO)_4$[c]	17.39	16.81	0.288	0.261	1.102	0.58
(18)	$Cl_3SnCo(CO)_4$[c]	17.71	17.19	0.257	0.254	1.014	0.52
		17.52	17.26	0.321	0.229	(1.4)	0.26
(19)	$Br_3SnCo(CO)_4$[c]	17.63	17.11	0.259	0.258	1.005	0.52
(20)	$I_3SnCo(CO)_4$[c]	17.53	17.01	0.259	0.248	1.045	0.52
(21)	$(C_6H_5)_3PFe(CO)_4$[d]	16.46	15.60	0.431	0.381	1.131	0.86
(22)	$(4\text{-}ClC_6H_4)_3PFe(CO)_4$[f]	16.44	15.67	0.383	0.343	1.116	0.77
(23)	$(4\text{-}FC_6H_4)_3PFe(CO)_4$[g]	16.41	15.64	0.385	0.338	1.139	0.77

[a] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, *6*, 981 (1967). [b] O. Kahn and M. Bigorgne, *J. Organometal. Chem.*, *10*, 137 (1967). [c] Frequencies from ref. 7. [d] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960). [e] Carbonyl stretching vibrations at 2091, 2033, 2010 and 1933 cm^{-1} in cyclohexane. [f] 2054, 1981 and 1946 cm^{-1}, in chloroform. [g] 2052, 1980, 1944 cm^{-1}, in chloroform.

TABLE II. Exact Force Constants for Some Phosphine Substituted Tricarbonylcobalt Tin(IV) Derivatives (mdynes/Å).

Compound	k_e	c'
$(C_6H_5)_3PCo(CO)_3SnBr_3$[a]	16.45	0.311
$(4\text{-}FC_6H_4)_3PCo(CO)_3SnBr_3$[b]	16.45	0.317
$(4\text{-}FC_6H_4)_3PCo(CO)_3SnCl_3$[c]	16.50	0.295
$(C_6H_5)_3PCo(CO)_3Sn(C_4H_9)Cl_2$[a]	16.19	0.358
$(C_6H_5)_3PCo(CO)_3Sn(C_6H_5)Cl_2$[a]	16.24	0.347

[a] Frequencies from ref. 7. [b] Carbonyl stretching modes at 2057 (vw) and 1999 (vs) cm^{-1}, in chloroform. [c] 2057 (vw) and 2003 (vs) cm^{-1}, in chloroform.

electron system of the phenyl ring and the empty 5*d* orbitals of tin.

Another measure of the inductive electron-withdrawing power of a substituent X may be estimated from the charge separation q_{C-X} obtained by dividing the bond moment μ_{C-X} by the interatomic distance r_{C-X} [6]. Within the series $(Ch_3)_{3-n}X_nSnCo(CO)_4$, X = Cl, Br, I, very good linear correlations between k_a and k_e and these q_{C-X} values were found. The correlation factors even reach 0.962 and 0.960 respectively.

When comparing the phosphine substituted derivatives (Table II) with their parent compounds in Table I, c' is found on average to increase by 0.05 mdynes/Å. k_e decreases by some 0.66 mdynes/Å. Both these changes indicate an increase of electron density on the transition metal. Such an increase of negative charge on cobalt may result from decreased π-acceptor or increased σ-donor ability of the phosphines relative to CO. The phosphines being good σ-donor ligands, is affirmed by the high $\Delta k_{a,e}$ values obtained for the phosphine substituted iron carbonyls (Table I).

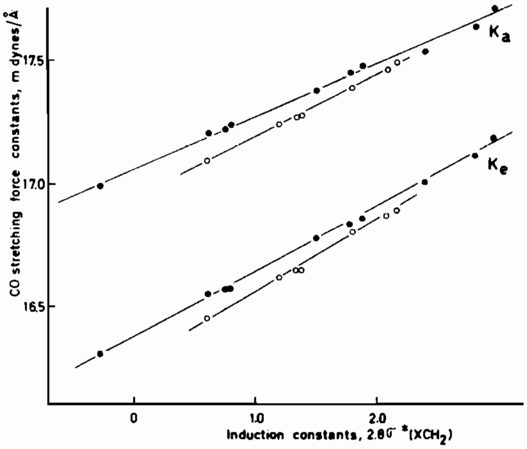

Figure. Plots of CO stretching force constants against Taft induction constants for $R_{3-n}X_nSnCo(CO)_4$ compounds, X = Cl, Br, I, R = CH_3 (●), C_6H_5 (○).

Experimental

The preparation of $(4\text{-}FC_6H_4)_3PCo(CO)_3SnBr_3$, $(4\text{-}FC_6H_4)_3PCo(CO)_3SnCl_3$ and of the compounds (5), (7), (11), (14), (22) and (23) closely followed published methods [7, 8]. The compounds (16) and (9) were prepared by treating 1 mmol of $Br_2(CH_3)SnCo(CO)_4$ or 2 mmol of $Br(CH_3)_2SnCo(CO)_4$ in acetone with 2 mmol of NaI in the same solvent. After filtration of the precipitated NaBr the solvent was removed under vacuum and the residue recrystallized twice from n-pentane with cooling. The infrared spectral data for the molecules $(CH_3)_{3-n}X_nSnCo(CO)_4$, X = Cl, Br, I, are described by the present authors elsewhere [9].

References

1 P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, 1975, p. 42.
2 J. Dalton, I. Paul, J. G. Smith and F. G. A. Stone, *J. Chem. Soc. A*, 1199 (1968).
3 D. J. Darensbourg, *Inorg. Chim. Acta, 4*, 597 (1970).
4 D. J. Darensbourg, H. H. Nelson, III, and C. L. Hyde, *Inorg. Chem., 13*, 2135 (1974).
5 R. W. Taft, in "Steric Effects in Organic Chemistry", ed. M. S. Newman, Wiley, New York (1956), p. 615.
6 L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, New York (1944), p. 64.
7 D. J. Patmore and W. A. G. Graham, *Inorg. Chem., 7*, 771 (1968).
8 H. L. Conder and M. Y. Darensbourg, *J. Organomet. Chem., 67*, 93 (1974).
9 L. F. Wuyts and G. P. Van der Kelen, *Spectrochim. Acta*, 1976, in press.