Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

TRANSITION METAL CHEMISTRY
III. A MORE EXACT METHOD FOR EVALUATION OF CO STRETCHING FORCE CONSTANTS OF PENTACARBONYL COMPLEXES OF TRANSITION METALS, BASED ON THE COTTON AND KRAIHANZEL FORCE FIELD

F. T. DELBEKE, E. G. CLAEYS, G. P. VAN DER KELEN AND R. M. DE CALUWE
Laboratory for General and Inorganic Chemistry, B, University of Ghent, Krijgslaan 105, 9000 Ghent (Belgium)

(Received February 19th, 1970)

SUMMARY

Within the framework of exact secular equations, a rigorous algebraic method for calculating all the CO stretching force constants of the complexes of general formula LM(CO)$_5$ is possible yielding at once all the solutions, whether physically acceptable or not. This method does not imply interation and there is no need for estimating good initial approximations.

SYMMETRY

Monosubstituted metal carbonyls of the type M(CO)$_5$L with M = Mo, W, Cr, Mn and Re belong to the molecular point group C_{4v}. For these compounds the theory predicts four CO stretching frequencies ($2\,A_1+E+B_1$); the A_1+E modes are both IR and Raman-active, whereas the B_1-mode only Raman-active.

CALCULATIONS OF FORCE CONSTANTS

Generally, the calculation of CO stretching force constants of metal carbonyls is based on the Cotton and Kraihanzel force field[1-3].

For the compounds of the type M(CO)$_5$L (Fig. 1) there are five CO stretching force constants (k_1, k_2, k_c, $k_{c'}$ and k_t) which must be evaluated from four vibration

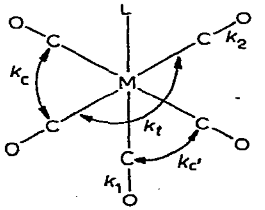

Fig. 1. The M(CO)$_5$L molecule and the CO stretching force constants.

frequencies. Therefore all calculations of force constants have been done previously using the Cotton and Kraihanzel approximation method. This method is based on the assumption that $k_c = k_{c'} = k_t/2 = k_i$.

The secular equations of the exact and approximation method for $M(CO)_5L$ compounds are presented in Tables 1 and 2.

TABLE 1

EXACT FORMULATION OF THE SECULAR EQUATIONS FOR $M(CO)_5L$ COMPOUNDS

A_1 (1)	$\mu \cdot k_1 - \lambda$	$2\mu \cdot k_{c'}$	$= 0$	(1)
A_1 (2)	$2\mu \cdot k_{c'}$	$\mu \cdot (k_2 + k_t + 2k_c) - \lambda$		(2)
B_1		$\lambda = \mu \cdot (k_2 + k_t - 2k_c)$		(3)
E		$\lambda = \mu \cdot (k_2 - k_t)$		(4)

TABLE 2

APPROXIMATE FORMULATION OF THE SECULAR EQUATIONS FOR $M(CO)_5L$ COMPOUNDS

A_1 (1)	$\mu \cdot k_1 - \lambda$	$2\mu \cdot k_i$	$= 0$
A_1 (2)	$2\mu \cdot k_i$	$\lambda \cdot (k_2 + 4k_i) - \lambda$	
B_1		$\lambda = \mu \cdot k_2$	
E		$\lambda = \mu \cdot (k_2 - 2k_i)$	

From the secular equations shown in Table 1 four equations in five unknowns are obtained and these necessarily result in an undetermined algebraic system. On the other hand, the number of force constants in the secular equations of the approximation method (Table 2) is reduced to three. This is obviously an oversimplification.

A better solution of the problem could be the assumption $k_c = k_{c'}$ (four equations, four force constants) but it appears from our results that the assumption is not realistic.

In a recent paper Dalton *et al.*[4,5] found some interesting relations [eqns. (5) and (6)] between the CO interaction force constants of $M(CO)_5L$ compounds. These relationships result from orbital overlap theories developed by Bedon *et al.*[6] and Kettle[7] and based on the work of Jones[8]:

$$\frac{k_{c'}}{k_c} = \frac{6}{2.4 + 1.4\,y} \tag{5}$$

$$\frac{k_t}{k_c} = \frac{6.2 + 1.4\,y}{2.4 + 1.4\,y} \tag{6}$$

Their method for evaluation of the CO stretching force constants consists in the combination of eqns. (5) and (6) with the secular equations of Table 1 in order to calculate both A_1-frequencies, which generally could be found respectively to within $\pm 1\ \text{cm}^{-1}$ and $\pm 4\ \text{cm}^{-1}$ when the ratios $k_{c'}/k_c$ and k_t/k_c were increased in small steps. It should be mentioned that such a procedure not only necessitates the estimation of good initial approximations but also gives rise to several solutions which are all compatible with the experimental data.

(*continued p.* 502)

TABLE 3

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS FOR PENTACARBONYL DERIVATIVES OF SOME TRANSITION METALS

Compound		Ref.	Frequencies (cm^{-1})				Force constants (mdynes/Å)				
			A_1 (1)	A_1 (2)	B_1	E	k_1	k_2	k_c	$k_{c'}$	k_t
(I)	$Ph_3PCr(CO)_5^a$	1	2070	1944	1989	1944	15.59_1	15.87_6	0.2547_6	0.3515_4	0.6063_1
(II)	$Ph_3PMo(CO)_5^a$	1	2078	1951	1990	1951	15.58_7	16.00_0	0.3097_3	0.3104_7	0.6202_1
(III)	$Ph_3PW(CO)_5^a$	1	2074	1943	1981	1943	15.43_0	15.89_2	0.3359_5	0.3028_8	0.6388_3
(IV)	$Et_3PMo(CO)_5^b$	9	2069	1947	1980	1941	15.53_2	15.84_1	0.3099_3	0.3089_8	0.6189_1
	$Et_3PMo(CO)_5^b$	4	2070	1941	1980	1948	15.32_7	15.93_0	0.3401_4	0.2576_3	0.5977_7
(V)	$Et_3AsMo(CO)_5^b$	10	2070	1943	1983	1943	15.47_7	15.87_0	0.3006_8	0.3164_0	0.6170_9
(VI)	$(MeO)_3PMo(CO)_5^b$	10	2080	1962	1993	1952	15.81_9	16.01_2	0.2924_3	0.3249_5	0.6173_8
(VII)	$(MeO)_3AsMo(CO)_5^b$	10	2088	1975	2006	1968	15.99_6	16.23_3	0.2806_9	0.3038_1	0.5845_1
(VIII)	$Cl_2(EtO)PMo(CO)_5^b$	10	2091	1985	2012	1976	16.14_6	16.33_6	0.2713_5	0.2890_8	0.5604_2
(IX)	$(C_6H_{11}NH_2)Cr(CO)_5^a$	2	2067	1890	1980	1935	16.64_0	15.78_7	0.3052_7	0.3531_9	0.6584_6
(X)	$(C_6H_{11}NH_2)Mo(CO)_5^a$	2	2072	1895	1983	1938	14.71_4	15.84_4	0.3145_3	0.3542_3	0.6687_6
(XI)	$(C_6H_{11}NH_2)W(CO)_5^a$	2	2071	1894	1974	1929	14.68_6	15.73_8	0.3484_2	0.3545_0	0.7029_3
(XII)	$Ph_3SiMn(CO)_5^c$	11	2098	2003	2030	2003	16.33_5	16.68_3	0.2516_1	0.2214_6	0.4730_7
(XIII)	$Ph_3GeMn(CO)_5^c$	11	2097	2002	2032	2006	16.30_9	16.71_4	0.2416_2	0.2134_8	0.4551_0
	$Ph_3GeMn(CO)_5^c$	4	2097	2006	2032	2002	16.44_5	16.66_3	0.2251_8	0.2434_8	0.4686_7
(XIV)	$Ph_3SnMn(CO)_5^c$	11	2093	2002	2027	2002	16.30_0	16.64_7	0.2471_7	0.2054_6	0.4526_4
(XV)	$Ph_3PbMn(CO)_5^c$	11	2091	2003	2029	2003	16.34_2	16.64_8	0.2247_0	0.2124_1	0.4371_1
(XVI)	$Ph_3SiRe(CO)_5^c$	11	2118	2003	2044	2012	16.36_4	16.89_2	0.2725_3	0.2627_2	0.5352_5
(XVII)	$Ph_3GeRe(CO)_5^c$	11	2118	2000	2047	2014	16.32_9	16.91_6	0.2573_4	0.2700_5	0.5274_0
(XVIII)	$Ph_3SnRe(CO)_5^c$	11	2114	2003	2042	2012	16.34_5	16.87_1	0.2680_1	0.2467_7	0.5147_8

(*continued*)

TABLE 3 (*continued*)

Compound		Ref.	Frequencies (cm^{-1})				Force constants (mdynes/Å)				
			A_1 (1)	A_1 (2)	B_1	E	k_1	k_2	k_c	$k_{c'}$	k_t
(XIX)	$Ph_3PbRe(CO)_5{}^c$	11	2114	2001	2044	2015	16.30_0	16.90_7	0.2630_0	0.2390_0	0.5020_0
(XX)	$Me_3SnRe(CO)_5{}^c$	4	2108	2003	2034	2003	16.36_7	16.73_4	0.2701_1	0.2536_6	0.5237_7
	$Me_3SnRe(CO)_5{}^c$	11	2108	2003	2014	2003	^{f}	^{f}	^{f}	^{f}	^{f}
(XXI)	$Me_2ClSnMn(CO)_5{}^c$	4	2101	2006	2039	2011	16.40_8	16.79_1	0.2222_3	0.2287_5	0.4509_7
(XXII)	$Br_3SnMn(CO)_5{}^c$	11	2122	2037	2060	2043	16.78_7	17.26_4	0.2545_6	0.1449_9	0.3995_4
(XXIII)	$Br_3SnMn(CO)_5{}^c$	4	2122	2043	2060	2037	16.97_1	17.19_2	0.2343_5	0.1923_4	0.4266_9
	$Cl_3SnRe(CO)_5{}^c$	11	2141	2030	2077	2044	16.84_3	17.37_9	0.2258_5	0.2720_5	0.4979_1
(XXIV)a.	$Br_3SnRe(CO)_5{}^c$	11	2143	2030	2070	2046	16.70_8	17.41_2	0.2943_0	0.2034_0	0.4977_1
b.	$Br_3SnRe(CO)_5{}^c$	4	2143	2030	2090	2046	^{g}	^{g}	^{g}	^{g}	^{g}
(XXV)	$C_2F_5Mn(CO)_5{}^d$	12	2130	2023	2072	2038	16.76_1	17.25_1	0.1925_2	0.2769_6	0.4694_8
(XXVI)	$HCF_2CF_2Mn(CO)_5{}^c$	13 14	2134	2015	2073	2042	16.55_9	17.32_5	0.2216_7	0.2557_7	0.4774_4
(XXVII)	$HCFClCF_2Mn(CO)_5{}^c$	13 14	2133	2014	2072	2040	16.55_6	17.29_7	0.2185_5	0.2632_4	0.4817_8
(XXVIII)	$HCF_2CFClMn(CO)_5{}^c$	13	2132	2014	2075	1044	16.55_0	17.33_9	0.2034_6	0.2549_1	0.4583_7
(XXIX)	$HCCl_2CF_2Mn(CO)_5{}^c$	14 15	2131	2013	2072	2040	16.54_4	17.28_7	0.2091_4	0.2626_6	0.4718_0
(XXX)	$C_2F_5Re(CO)_5{}^d$	12	2145	2013	2075	2038	16.57_6	17.33_5	0.2492_3	0.3042_3	0.5534_5
(XXXI)	$C_3F_7Re(CO)_5{}^d$	12	2146	2014	2078	2039	16.62_4	17.35_1	0.2339_1	0.3191_2	0.5530_3
(XXXII)	$HCFClCF_2Re(CO)_5{}^c$	13 16	2147	2011	2075	2037	16.54_8	17.33_5	0.2568_2	0.3124_3	0.5692_4
(XXXIII)	$HCCl_2CF_2Re(CO)_5{}^c$	13	2147	2011	2074	2037	16.53_2	17.33_5	0.2644_1	0.3049_9	0.5693_9
(XXXIV)	*cis*-$CFH{=}CFMn(CO)_5{}^e$	17	2132	2014	2071	2037	16.58_6	17.25_5	0.2116_7	0.2781_4	0.4998_1

(XXXV)	$C_4F_5Mn(CO)_5$[c]	18	2132	2010	2073	2039	16.51_7	17.28_1	0.2046_5	0.2779_3	0.4825_8
(XXXVI)	CF_2=CFRe$(CO)_5$[c]	19	2145	2002	2065	2040	16.23_0	17.35_6	0.3290_2	0.2120_5	0.5410_6
(XXXVII)	*trans*-CF_3CF=CFRe$(CO)_5$	19	2143	2015	2065	2045	16.40_5	17.39_8	0.3289_4	0.1715_6	0.5005_0
(XXXVIII)	*cis*-CF_3CH=CHRe$(CO)_5$[c]	20	2143	1998	2070	2029	16.36_2	17.22_4	0.2550_2	0.3347_0	0.5897_1
(XXXIX)	CF_2=C=C(CF_3)Re$(CO)_5$[c]	18	2148	2012	2070	2042	16.43_1	17.39_6	0.3120_9	0.2360_0	0.5481_0
(XL)	$C_4F_5Re(CO)_5$[c]	18	2144	2012	2073	2038	16.53_0	17.33_1	0.2598_0	0.2890_5	0.5488_4
(XLI)	$C_8F_{11}H[Re(CO)_5]_2$[c]	18	2148	2012	2070	2045	16.39_9	17.42_9	0.3194_0	0.2122_4	0.5316_5
(XLII)	cyclo-$C_4F_5Mn(CO)_5$[c]	19 21	2134	2022	2070	2048	16.57_0	17.39_1	0.2575_2	0.1861_3	0.4436_5
(XLIII)	cyclo-$C_6F_9Mn(CO)_5$[c]	19 21	2137	2020	2075	2047	16.60_4	17.39_8	0.2344_2	0.2332_3	0.4676_5
(XLIV)	$NC_5F_4Mn(CO)_5$[c]	22 23	2132	2015	2068	2042	16.49_6	17.31_3	0.2481_9	0.2173_9	0.4655_7
(XLV)	$N_3C_3F_2Mn(CO)_5$[c]	23	2130	2018	2062	2043	16.46_8	17.30_9	0.2821_2	0.1620_5	0.4441_8
(XLVI)	$NC_5F_4Re(CO)_5$[c]	22 23	2146	2010	2068	2037	16.43_2	17.32_9	0.3039_6	0.2592_3	0.5631_9

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[a] In chloroform. [b] In n-hexadecane. [c] In cyclohexane. [d] In tetrachloroethylene. [e] In nujol-mull. [f] Physically unacceptable force constants. [g] Negative y values.

In contrast, combination of the secular equations of Cotton and Kraihanzel in their exact formulation with the relationships (5) and (6) allows the solution of this system by gradually eliminating the various unknowns. In this way one arrives at a resolvent algebraic equation of the second degree in the unknown y, giving two sets of values for the force constants in perfect accordance with the spectroscopic data. It is evident that one of these sets must be physically acceptable. Nevertheless, using eqns. (5) and (6) the two values of y thus found are both negative. Since y is a factor related to the change in π-overlap integral occurring on the replacement of a CO group by L in a metal carbonyl ($S_i \rightarrow y \cdot S_i$), it cannot be negative.

It is, however, important to note that the eqns. (5) and (6) were derived from the relationships expressed by eqns. (7) and (8), by introducing angular correction terms in the treatment of Jones[24].

$$\frac{k_{c'}}{k_c} = \frac{3}{2+y} \tag{7}$$

$$\frac{k_t}{k_c} = \frac{5+y}{2+y} \tag{8}$$

We therefore also combined the exact Cotton and Kraihanzel secular equations with the eqns. (7) and (8) to derive the second degree equation in y. We found negative and positive y roots, the latter resulting in physically meaningful sets of values for the force constants (Table 3).

Furthermore, when the values of force constant k_c, $k_{c'}$ and k_t thus obtained are used to recalculate values of y using relationships (7) and (8), equal values of y are found for one and the same compound, irrespective of the equation used for the calculation.

The calculations were mainly carried out in double precision on the IBM 360 type 30 computer of the Computing Laboratory of the University of Ghent, Director Prof. Dr. C. C. Grosjean.

DISCUSSION

The assignment of the frequencies of compound (IV) made by Dalton *et al.*[4] differs from that given by Poilblanc and Bigorgne[9]. By analogy with $Et_3AsMo(CO)_5$ and $PPh_3Mo(CO)_5$ we prefer the assignment of Bigorgne. There are also two possible assignments for $Ph_3GeMn(CO)_5$ [compound (XIII)] arising from interchanging the $A_1(2)$ and E-modes. By the analogy with other compounds we choose the assignment of Jetz *et al.*[11] and not that of Dalton[4]. The B_1-mode of compound (XXIVb) given by Dalton *et al.*[4] could be erroneous, as we found two negative values of y. As cited by Dalton[4] it is assumed that the B_1-mode of compound (XX) occurs at 2034 cm^{-1} and not at 2014 cm^{-1} as reported by Jetz *et al.*[11].

In the Cotton and Kraihanzel force field the axial stretching force constant k_1 must always be less than the radial one k_2. In the work of Dalton *et al.*, however, some results are still contrary to this condition. They conclude therefore that either their CO stretch-stretch interactions are erroneous or the CK-force field restriction ($k_2 > k_1$) must be waived and they prefer the second conclusion. On the contrary, using eqns. (7) and (8) instead of the relationships given by Dalton we found force constants which are in complete agreement with the Cotton and Kraihanzel restriction; therefore we must conclude that after all the relationships (5) and (6) could be erroneous.

Finally, it should be obvious that a more exact approximation for calculation of CO stretching force constants of $LM(CO)_5$ type of compounds consists in simply assuming $k_c + k_{c'} = k_t$.

ACKNOWLEDGEMENT

The authors wish to thank Dr. J. Dalton for some kind information.

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