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A STUDY OF VIBRATIONAL FORCE CONSTANTS IN SOME TRANSITION METAL—ETHYLENE π-COMPLEXES

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Summary

Approximate force-fields have been calculated for the complex-fragments $(C_2H_4)Fe$ and $(C_2H_4)Pt$. The metal—ligand bonding is much stronger in the latter case, as shown by the larger value of f(M—C) and the smaller value of f(C=C). Many of the normal modes were shown to be derived from more than one type of internal coordinate, and hence the vibrational wavenumbers themselves are of limited value in discussions of bonding in such molecules.

As the simplest organic molecule capable of forming π-complexes with transition metals, ethylene is of particular interest to organometallic chemists [1]. One of the methods by which the bonding in olefin—metal complexes has been studied most frequently is vibrational spectroscopy [2]. However, use of vibrational wavenumbers as indicators of the extent of metal—olefin interaction has been hindered by disagreements as to the correct vibrational assignments, especially for ν(C=C) in Zeise's salt, $K[(C_2H_4)PtCl_3] \cdot H_2O$ [3,4,5]. This problem has been shown to arise from extensive mixing of internal coordinates in the normal modes, chiefly involving C=C stretching and CH_2 symmetric deformation ("scissors") [6]. Consequently it is necessary to subject the coordinated ethylene molecule to a normal coordinate analysis, with the aim of determining as realistic a vibrational force field as possible. Some such attempts have been made previously for Zeise's salt [6,7].

Quite complete vibrational data are now available for the $(C_2H_4)Fe$ fragment of $(C_2H_4)Fe(CO)_4$ [8], and the present paper describes the results of normal coordinate analyses for $(C_2H_4)Fe$ and $(C_2H_4)Pt$, using an approximation to the General Valence Force Field (GVFF). An indication of the perturbation of the force field of ethylene on complexing will be given by comparison with data for the free molecule. Two detailed calculations based upon experimental vibrational results [9,10], and one determination of a GVFF from ab initio MO calculations [11] are available, although accurate comparisons will not always be possible be-

TABLE 1

VIBRATIONAL ASSIGNMENTS FOR $(C_2H_4)M$, ALL FIGURES IN CM^{-1}

		M	
		Fe	Pt
A_1			
	CH_2 stretch	2970	3013
	CH_2 deformation }	1511	1515
	C=C stretch }	1193	1243
	CH_2 wag	940	975
	(C_2H_4)—M stretch	356	405
A_2			
	CH_2 stretch		3079
	CH_2 rock		
	CH_2 twist	798	841
B_1			
	CH_2 stretch	2930	2988
	CH_2 deformation	1445	1426
	CH_2 wag	1033	1010
	(C_2H_4)—M stretch	400	493
B_2			
	CH_2 stretch	3080	3094
	CH_2 rock	708	841

cause of the use of different sets of internal and symmetry coordinates in these studies.

Experimental

The vibrational wavenumbers for the $(C_2H_4)Fe$ fragment were taken from the work of Andrews and Davidson on $(C_2H_4)Fe(CO)_4$ [8], those for $(C_2H_4)Pt$ from Hiraishi's assignment for Zeise's salt [4]. The wavenumbers and suggested assignments are given in Table 1. The structural parameters [12,13] are given in Table 2.

The internal coordinates used are illustrated in Fig. 1, and the symmetry coordinates listed in Table 3. It was considered appropriate to include both HCH

TABLE 2

STRUCTURAL PARAMETERS FOR $(C_2H_4)M$.

	M	
	Fe	Pt
r(C—H)	1.08 Å	1.08 Å
r(C=C)	1.46 Å	1.42 Å
r(M—C)	2.12 Å	2.18 Å
∠H—C—C	122.0°	122.0°
∠C—C—M	69.8°	71.0°

TABLE 3

SYMMETRY COORDINATES FOR THE SYSTEM $(C_2H_4)M$

A_1

$S_1 = ½(\Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4)$
$S_2 = 1/\sqrt{6}(\Delta\beta_1 + \Delta\beta_2 - \Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_4)$
$S_3 = \Delta t$
$S_4 = 1/\sqrt{2}(\Delta\gamma_1 + \Delta\gamma_2)$
$S_5 = 1/\sqrt{2}(\Delta R_1 + \Delta R_2)$
$S_6 = 1/2\sqrt{2}(2\Delta\beta_1 + 2\Delta\beta_2 + \Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4)$

A_2

$S_7 = ½(\Delta s_1 - \Delta s_2 - \Delta s_3 - \Delta s_3 + \Delta s_4)$
$S_8 = ½(\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 + \Delta\alpha_4)$
$S_9 = \Delta\tau$

B_1

$S_{10} = ½(\Delta s_1 + \Delta s_2 - \Delta s_3 - \Delta s_4)$
$S_{11} = 1/\sqrt{6}(\Delta\beta_1 - \Delta\beta_2 - \Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4)$
$S_{12} = 1/\sqrt{2}(\Delta\gamma_1 - \Delta\gamma_2)$
$S_{13} = 1/\sqrt{2}(\Delta R_1 - \Delta R_2)$
$S_{14} = 1/2\sqrt{2}(2\Delta\beta_1 - 2\Delta\beta_2 + \Delta\alpha_1 + \Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_4)$

B_2

$S_{15} = ½(\Delta s_1 - \Delta s_2 + \Delta s_3 - \Delta s_4)$
$S_{16} = ½(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4)$

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and HCC angles in the former set, introducing two angle bending redundancies in the latter set. The alternative possibility [11], of defining only the H—C—C angle, leads to excessively large values for the *geminal* H—C—C bend—bend interaction force constant.

The programs used in the course of the calculation were firstly, those described by Schachtschneider [14], and secondly (in the later stages) a new program which will be described fully elsewhere [15]. This is based upon an algorithm due to Marquardt [16].

The strategy employed in the calculations was closely similar to that described in the normal coordinate analyses of (cyclobutadiene)iron tricarbonyl [17] and (trimethylenemethane)iron tricarbonyl [18]. Thus, a model of an isolated C_2H_4 molecule of C_{2v} symmetry was used as an initial approximation, with a simple valence force field (no interaction terms). Interaction terms were added successively (up to the limit imposed by the number of observed vibrational wavenumbers) to improve the fit between calculated and observed wavenumbers for C_2H_4 modes in $(C_2H_4)Fe(CO)_4$, being discarded if no improvement occurred. The final force field obtained by this procedure, which was able to reproduce all of the C_2H_4 wavenumbers except the A_1 C—H stretch (error 3 cm^{-1}) to ±1 cm^{-1}, was then transferred, with necessary additions, to the $(C_2H_4)M$ model of Fig. 1 (M = Fe initially). The same process was followed to obtain an accurate fit for the wavenumbers and the resulting force field was able to reproduce all of the $(C_2H_4)Fe$ wavenumbers to well within 1 cm^{-1}.

To obtain a similar force field for $(C_2H_4)Pt$ the final force field so obtained for $(C_2H_4)Fe$ was used as the starting point, and refined further to reproduce the wavenumbers exactly.

In each case, some force constants had to be held at fixed, non-zero values — their optimum values being determined by running the problems with series of such fixed values.

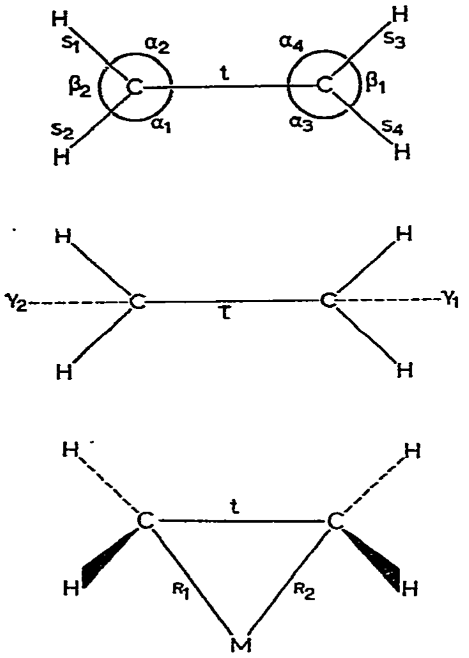

Fig. 1. Internal coordinates for $(C_2H_4)M$; (γ_1,γ_2 refer to CH_2 wagging, τ to the CH_2 twisting coordinates).

Results and discussion

The final force fields obtained for $(C_2H_4)Fe$ and $(C_2H_4)Pt$ are listed in Table 4, all other force constants being fixed at zero. The units in which the force constants are expressed are: (a) stretching, and stretch—stretch interactions, mdyn $Å^{-1}$; (b) bending, and bend—bend interactions, mdyn Å rad^{-2}, and (c) stretch—bend interactions, mdyn rad^{-1}.

Comparison of the force constants with analogous ones of free C_2H_4 reveals that the greatest change, as expected, has occurred in the C=C stretching force constant. There are slight differences in the reported values of this in C_2H_4 [9-11], but all agree that it is >9 mdyn $Å^{-1}$. For the $(C_2H_4)Fe$ model it is 6.14 mdyn $Å^{-1}$, and for $(C_2H_4)Pt$ 4.23 mdyn $Å^{-1}$. These decreases are in accord with the Dewar—Chatt bonding model, in which donation of ethylene π-bonding electrons to the metal, and back-donation of electrons from the metal to the ethylene π^*-orbitals both weaken the C=C bond [19]. In addition, the extent of the metal—ethylene bonding interaction is clearly much greater for the Pt system than for $(C_2H_4)Fe$, which is in agreement with the known relative stabilities of $[(C_2H_4PtCl_3]^-$ and $(C_2H_4)Fe(CO)_4$.

The same conclusion follows from the values of the M—C stretching force constants, i.e. 1.76 mdyn $Å^{-1}$ for M = Fe, and 3.34 mdyn $Å^{-1}$ for M = Pt.

The formal oxidation state of the Pt in Zeise's salt is +2 while that of Fe in $(C_2H_4)Fe(CO)_4$ is 0. Coupled with the fact of stronger ethylene—metal bonding in the former case this suggests that the dominant bonding mechanism is ethylene→metal σ-donation, rather than metal→ethylene π-back donation. This conclusion agrees with that of Rösch et al., based upon an SCF-MO calculation for $[(C_2H_4)PtCl_3]^-$ [20].

Other diagonal force constants associated with the ethylene fragment are rather similar in value for free C_2H_4 and for both $(C_2H_4)M$ systems. Comparison of $f(CH_{str.})$ is difficult since the calculated values for C_2H_4 itself are discrepant (5.17 mdyn $Å^{-1}$ [9], 5.60 mdyn $Å^{-1}$ [10]), and the values for the complexes lie between these (5.35 mdyn $Å^{-1}$, Fe; 5.47 mdyn $Å^{-1}$, Pt). Values for all of the angle bending diagonal force constants are (where comparisons can be made) closely similar in the free and complexed ethylene. Since the C=C stretching force constant indicates a considerable alteration in the bonding within the ethylene molecule as a result of complexation, this observation is perhaps surprising.

Turning to the interaction force constants, those involving two bending internal coordinates, and all except one of those involving two stretching coordinates, are rather small, and difficult to rationalise. The exception is f_{tR} (ca. 1.5 mdyn $Å^{-1}$ in each case), and this may be explained satisfactorily in terms of the Dewar—Chatt bonding model. The sign of this interaction indicates that if either C=C or M—C is stretched, the other bond becomes more difficult to stretch, and this is reasonable, since a greater M—C distance implies a smaller disruption of the ethylene bonding, and a higher effective C—C bond order. Increasing the C—C distance, conversely, implies a greater interaction with the metal, i.e. stronger bonding, and the M—C bond will exert a greater restoring force opposing vibration.

The two stretch—bend interactions included in the set of force constants

TABLE 4

THE FORCE FIELDS OBTAINED FOR $(C_2H_4)M$

	M	
	Fe	Pt
f_t	6.14	4.23
f_s	5.35	5.47
f_R	1.76	3.34
f_{s_1,s_2}	0	−0.02
f_{s_1,s_3}	0	0.007
f_{s_1,s_4}	0.04	0.01
$f_{t,R}$	1.46	1.59
f_α	0.53	0.45
f_β	0.40	0.50[a]
f_γ	0.29	0.28
f_τ	0.086	0.096
f_{α_1,α_3}	−0.11	0.07
f_{γ_1,γ_2}	0.03[a]	0.07[a]
f_{t,α_1}	0.22	0.21
f_{s_1,α_2}	−0.50	0.22

[a] Held at fixed values. All other force constants were constrained to be zero.

TABLE 5

DIAGONAL ELEMENTS OF THE POTENTIAL ENERGY DISTRIBUTION FOR $(C_2H_4)Fe$

	$\nu(\text{cm}^{-1})$	f_t	f_s	f_α	f_β	f_γ	f_T	f_R
A_1	2970		0.98					
	1510	0.56		0.23	0.15			
	1193	0.12	0.05	0.47	0.30			
	940	0.06				0.87		
	356	0.95						1.60
A_2	798						1.00	
B_1	2930		1.00					
	1445			0.57	0.38			
	1033					0.99		0.11
	400					0.12		0.89
B_2	3080		0.98					
	708		0.16	1.42				

for these calculations (f_{t,α_1} and f_{s_1,α_2}) both have values close to those in the free ethylene molecules, with the exception of f_{s_1,α_2} for $(C_2H_4)Pt$. Bearing in mind the approximations inherent in this model, however, it is difficult to comment on the physical significance of this.

Potential energy distributions in $(C_2H_4)Fe$ and $(C_2H_4)Pt$.

The chief reason for the disputes concerning vibrational assignments for Zeise's salt [3-5] is the extensive mixing of internal coordinates in the vibrational normal modes. An estimate of the magnitude of this mixing may be made by considering the diagonal elements of the potential energy distribution, i.e. $L_{ji}^2F_{jj}/\lambda_i$, where F_{jj} is a valence force constant, and L_{ji} is the associated eigenvector for any normal mode of wavenumber $\nu_i = \lambda_i^{1/2}N^{1/2}/2\pi C$, for which ν_i is in cm^{-1}, N is Avogadro's number, and all masses are expressed in atomic units. These diagonal elements are listed for each of the normal modes of $(C_2H_4)M$ in Tables 5 (M = Fe) and 6 (M = Pt) and elements less than 0.05 are omitted.

As expected, for both species the modes giving bands ca. 3000 cm^{-1} are entirely due to C—H stretching, but for some other modes more than one type

TABLE 6

DIAGONAL ELEMENTS OF THE POTENTIAL ENERGY DISTRIBUTION FOR $(C_2H_4)Pt$

	$\nu(\text{cm}^{-1})$	f_t	f_s	f_α	f_β	f_γ	f_T	f_R
A_1	3013		0.97					
	1515	0.15		0.25	0.56			
	1243	0.27		0.05	0.12	0.08		0.13
	975	0.16				0.69		
	405	1.03						1.42
A_2	3079		1.01					
	841						1.00	
B_1	2988		0.99					
	1426			0.32	0.72			
	1010					0.95		0.29
	493					0.39		0.71
B_2	3094		1.00					
	841			0.88				

of normal mode is involved. This is particularly marked in the A_1 block, where the bands ca. 1500 cm^{-1} and ca. 1200 cm^{-1} are both due to a mixture of CH_2 deformation and C=C stretching. In accordance with the values of f(C=C) discussed above, the Fe complex gives a larger contribution from C=C stretching in the higher-wavenumber mode. These results confirm those of Powell et al. [5] concerning the natures of these modes.

It should be noticed, finally, that the band at 356 cm^{-1} (M = Fe), 405 cm^{-1} (M = Pt) is derived from a mode involving both M—C and C=C stretching. The close relationship between these two types of motion was explained above.

Conclusion

An approximation to the GVFF has been achieved for the π-complexed fragments $(C_2H_4)Fe$ and $(C_2H_4)Pt$, which are able to reproduce their observed vibrational wavenumbers. It has become clear that even such approximate data as these are preferable to vibrational wavenumbers in discussions of the bonding in such systems, and they reveal that Pt^{II} is able to interact with the C_2H_4 molecule much more strongly than Fe^0, suggesting that (ethylene)→M donation is the dominant factor in bonding.

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