An Infrared Study of the Interaction of Substituted Ferrocenes with Phenols

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ABSTRACT. Infrared studies of the interaction of acetyl-, carboxaldehyde- and benzoyl-ferrocenes with phenols have shown that the acid base interaction, measured both as the change in O–H stretching frequency and the C=O stretching frequency, are related to the Hammett constant of the phenol. The change in O–H and C=O stretching frequencies are not necessarily linearly related when the groups attached to C=O are significantly different in mass.

There have been extensive studies of Lewis acid-base interactions involving phenols as hydrogen bonding acids (Drago and Epley 1967, 1969; Drago and Vogel 1970; Wettermark *et al.* 1973). The studies have involved bases having oxygen and nitrogen (Drago and Epley 1967, 1969; Wettermark *et al.* 1973) and sulphur donors (Drago and Vogel 1970). Few acid-base studies have involved organometallic compounds (Fisher and Ezeani 1983). We decided to study the basic properties of organometallic compounds having a group with a potential donor atom. The basicity of the group could then be compared with similar groups in organic compounds.

For this study, we decided to investigate the basicity of the carbonyl oxygen in three substituted ferrocene derivatives. The infrared technique has been used extensively to study the interaction of bases with phenols. Drago and Epley (1967) showed the linear relationship of the shift in the O–H stretching frequency of phenols with the enthalpy of the acid-base interaction

$$- \varDelta H = 0.0103 \, \varDelta\nu_{OH}(cm^{-1}) + 3.08$$

The substituted ferrocenes chosen have a carbonyl, C=O, group which may also be monitored. Drago *et al.* (1968) has studied the change in C=O stretching frequency of bases with acids. The substituted ferrocenes have the added advantage that they are air stable, easily prepared pure and are soluble in suitable solvents such as carbon tetrachloride. Carbon tetrachloride has been used extensively in infrared studies with phenols and alcohols such as 1,1,1,3,3,3-hexafluoro-2-propanol and 2,2,2-trifluoroethanol (Purcell *et al.* 1969, Purcell and Sherry (1970).

Experimental

Preparation of Pure Substituted Ferrocenes

a) Acetylferrocene $(C_5H_4COCH_3)Fe(C_5H_5)$

Acetylferrocene was prepared by the reaction of ferrocene with acetic anhydride, using phosphoric acid as catalyst. The crude product was purified by column chromatography using silica gel; petroleum ether, benzene mixtures were used to elute first unreacted ferrocene then acetylferrocene. The acetylferrocene was further purified by sublimation.

b) Benzoylferrocene $(C_5H_4COC_6H_5)Fe(C_5H_5)$

Benzoylferrocene was prepared by the reaction of ferrocene with benzoyl chloride in the presence of aluminium trichloride using carbon disulphide as solvent. The crude product was purified by column chromatography using aluminium oxide; petroleum ether, benzene mixtures were used first to elute unreacted ferrocene and then benzoylferrocene. The benzoylferrocene was further purified by sublimation.

c) Carboxaldehydeferrocene $(C_5H_4CHO)Fe(C_5H_5)$

Carboxaldehydeferrocene was prepared by the reaction of ferrocene with *N*-methylformanilide, using phosphorus oxychloride as catalyst. The crude product was purified by column chromatograph followed by sublimation.

Phenols

Most phenols were purifed by sublimation, except phenol which was distilled and allowed to cool and crystallize. The purified phenol was stored in a desiccator.

Solvents and Solutions

Carbon tetrachloride was distilled and stored over 4A molecular sieves. Solutions were prepared in previously dried volumetric flasks. Standard solutions of phenols and ferrocene derivatives were prepared and known volumes mixed to prepare known concentration solutions for infrared analysis.

Infrared Studies

Perkin Elmer 257 and 1330 Spectrophotometers were used. These instruments have a scale expansion capability of X2.5, X5 and X10. A variable pathlength cell was used, normally with a pathlength of 2 mm. Solution concentrations of 1×10^{-3} were generally used. Free phenol peaks were generally sharp but the peaks of the adducts were often broad, $\Delta \nu_{OH}$ was taken as the difference of the peak maxima. The CO peaks were sharp for both the free ferrocene and the adducts and so peak maxima were easily measured.

Results

The frequency shifts (5 cm^{-1}) for the O–H stretching for phenols and alcohols complexed with acetylferrocene are shown in Table 1 along with the C=O frequency shifts. Table 2 shows similar frequency shifts for the interactions with

Table 1. Frequency shifts observed for interactions of phenols with acetylferrocene in carbon tetrachloride solution.

Acid	$\Delta \nu_{OH}$ (cm^{-1})	$\Delta \nu_{CO}$ (cm^{-1})
Phenol	285	23
4-chlorophenol	300	27
4-bromophenol	305	26
4-iodophenol	312	27.5
4-methylphenol	270	22
4-nitrophenol	386	31
1,1,1,3,3,3-hexafluoro-2-propanol	370	26
2,2,2-trifluoroethanol	240	18

Table 2. Frequency shifts observed for interactions of phenols with benzoylferrocene in carbon tetrachloride solution.

Acid	$\Delta \nu_{OH}$ (cm^{-1})	$\Delta \nu_{CO}$ (cm^{-1})
Phenol	274	24.5
4-chlorophenol	300	26
4-bromophenol	295	26.5
4-iodophenol	310	27
4-methylphenol	255	23
4-nitrophenol	385	32
1,1,1,3,3,3-hexafluoro-2-propanol	320	25
2,2,2-trifluoroethanol	245	17

Table 3. Frequency shifts observed for interactions of phenols with carboxaldehyde ferrocene in carbon tetrachloride solution.

Acid	$\Delta\nu_{OH}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
Phenol	252	28
4-chlorophenol	280	29
4-iodophenol	285	29
4-methylphenol	246	27
4-nitrophenol	370	32
4-fluorophenol	270	28.5
1,1,1,3,3,3-hexafluoro-2-propanol	337	30
2,2,2-trifluoroethanol	215	19

benzoylferrocene. Table 3 shows the shifts for the interactions with carboxaldehydeferrocene.

Although the sharpness of the CO bands was such that the $\Delta\nu_{C=O}$ could be measured to 0.1 cm^{-1}, the values in the tables are quoted to 0.5 cm^{-1}.

Equilibrium studies with phenol and 4-chlorophenol (the $\Delta\nu_{OH}$ showing Beers law dependence) indicated equilibrium constants of approximately 50 for both the acetyl and benzoylferrocenes.

Figures 1, 2 and 3 show the relationship of $\Delta\nu_{OH}$ for the substituted ferrocenes with the Hammett constant σ of the substituted phenols. Figures 4, 5 and 6 show the relationships of $\Delta\nu_{C=O}$ with σ. Figures 7, 8 and 9 indicate the relationship of $\Delta\nu_{OH}$ and $\Delta\nu_{C=O}$ for the substituted ferrocenes. Linear correlation coefficients are given for each of the graphs.

Discussion

Previous studies by Drago and Epley (1967, 1969) have shown that the frequency shifts $\Delta\nu_{OH}$ of substituted phenols are linearly related to the Hammett constant σ. Wettermark *et al.* (1973) thoroughly investigated the interaction of a large number of phenols with N,N-dimethylacetamide and also found a good correlation of $\Delta\nu_{OH}$ with σ.

Using only *para* substituted phenols, to avoid steric interactions, our results shown in Fig. 1, 2 and 3 indicate that substituted ferrocene derivatives with ketonic oxygen donors have a similar interaction to that of organic oxygen and nitrogen donors. The graphs of $\Delta\nu_{OH}$ and σ indicate a linear dependence, the results for benzoylferrocene being slightly better than those for the acetyl and carboxaldehyde-ferrocene, as shown by the linear correlation coefficients. The graphs of
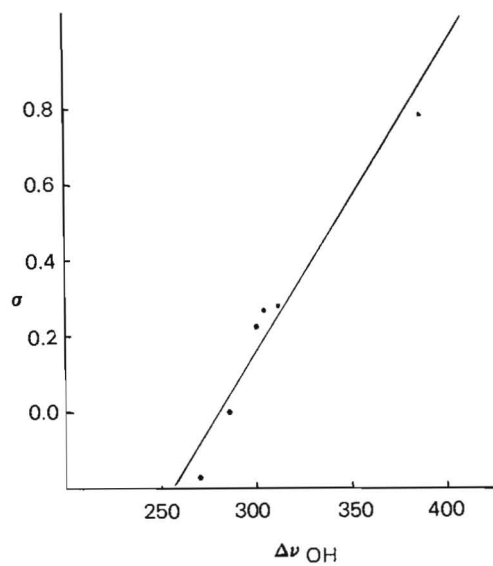
Fig. 1. A plot of σ vs $\Delta\nu_{OH}$ for acetylferrocene interacting with phenols. Linear correlation coefficient 0.9764.
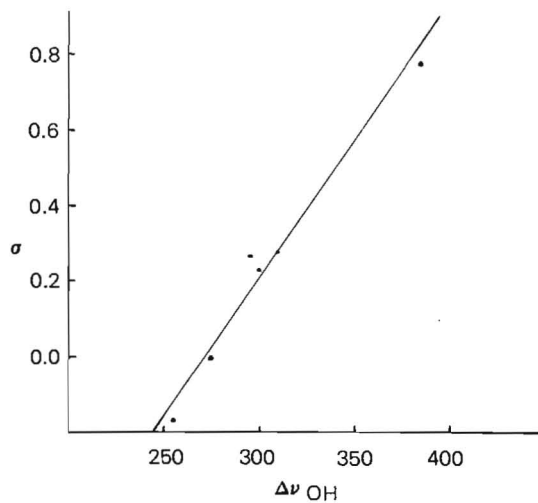

Fig. 2. A plot of σ vs $\Delta\nu_{OH}$ for benzoylferrocene interacting with phenols. Linear correlation coefficient 0.9855.
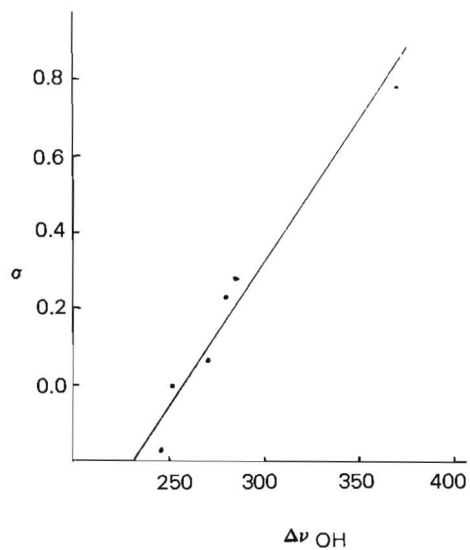
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Fig. 3. A plot of σ vs $\Delta\nu_{OH}$ for carboxaldehydeferrocene interacting with phenols. Linear correlation coefficient 0.9794.
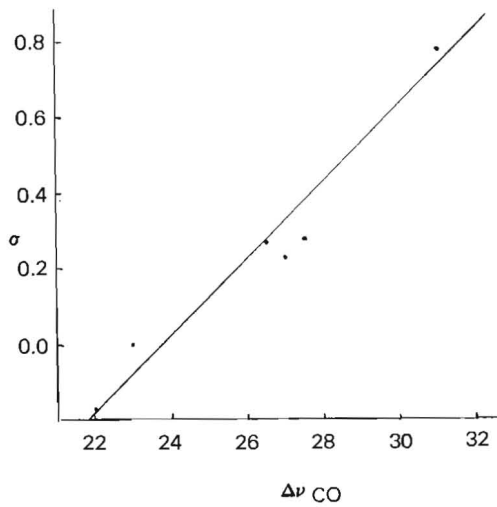

Fig. 4. A plot of σ vs $\Delta\nu_{CO}$ for acetylferrocene interacting with phenols. Linear correlation coefficient 0.9727.
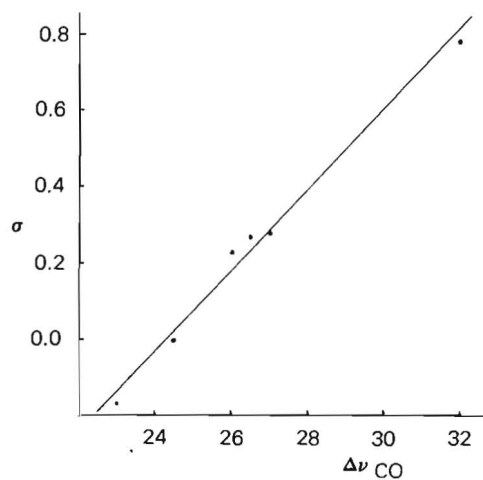
Fig. 5. A plot of σ vs $\Delta\nu_{CO}$ for benzoylferrocene interacting with phenols. Linear correlation coefficient 0.9937.
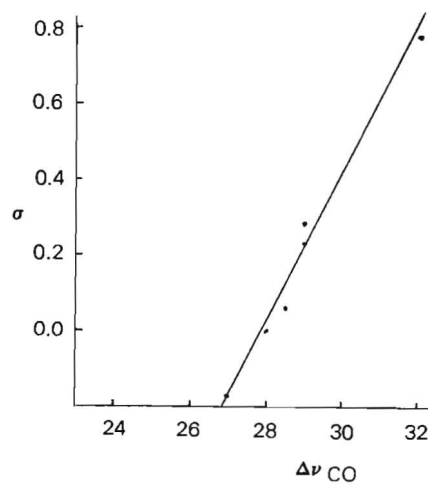

Fig. 6. A plot of σ vs $\Delta\nu_{CO}$ for carboxaldehydeferrocene interacting with phenols. Linear correlation coefficient 0.9921.

$\Delta\nu_{C=O}$ and σ, Fig. 4, 5 and 6, also show a linear dependence with the benzoyl results being slightly better. An interesting observation is that although the linear correlation coefficient is good for the change of $\Delta\nu_{C=O}$ of carboxaldehydeferrocene with σ, the changes are much smaller, and the spread of results is only 5 cm^{-1} versus 8 cm^{-1} for acetylferrocene.

Thus, it appears that both the change in O–H stretching frequency for the phenols and the C=O stretching frequency for the substituted ferrocenes are linearly related to the Hammett constant. The relationship of $\Delta\nu_{OH}$ and $\Delta\nu_{C=O}$ seems to be less well defined as shown in Fig. 7, 8 and 9. The linear correlation coefficient for the benzoyl substituent is again much better than for the acetyl and carboxaldehyde derivatives.

According to Drago *et al.* (1968), in his study of ethyl acetate adducts, "the C=O vibration is a highly localized one; but the amount of electron density drained from the CO bond when forming the adduct does not necessarily have a linear relationship to the strength of the adduct bond formed". Although a localized vibration there must be some effect of change of the relative masses and electronic properties of the attached groups. If we regard the ferrocene group as an aromatic group then the most symmetrical molecule (electronically and with respect to the masses of the attached groups to CO) is benzoylferrocene.
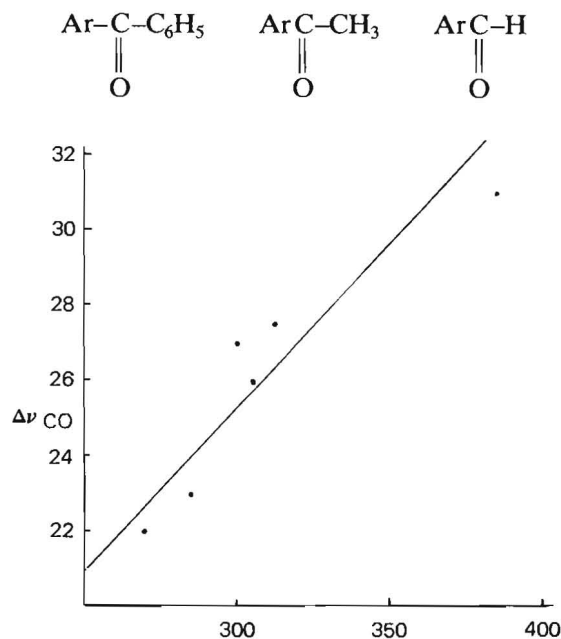

Fig. 7. A plot of $\Delta\nu_{CO}$ vs $\Delta\nu_{OH}$ for acetylferrocene interacting with phenols. Linear correlation coefficient 0.9247.

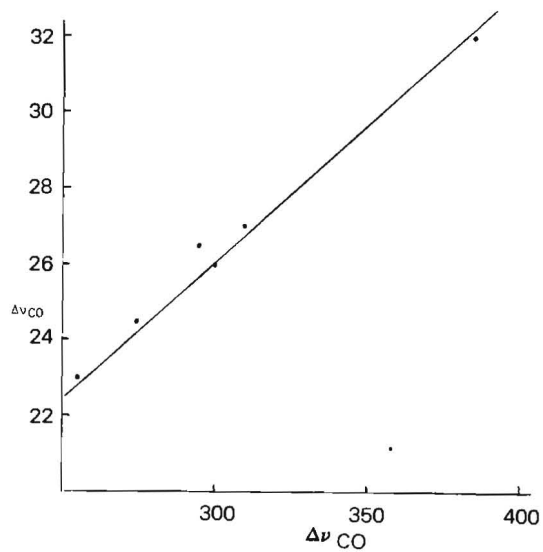**Fig. 8.** A plot of $\Delta\nu_{CO}$ vs $\Delta\nu_{OH}$ for benzoulferrocene interacting with phenols. Linear correlation coefficient 0.9953.
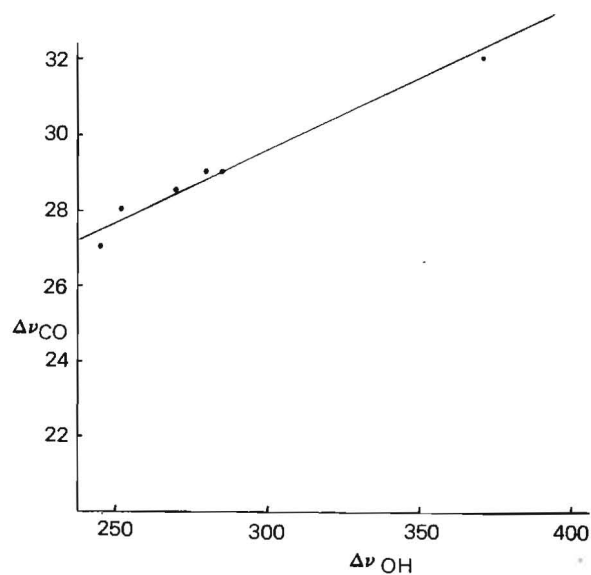

Fig. 9. A plot of $\Delta\nu_{CO}$ vs $\Delta\nu_{OH}$ for carboxaldehydeferrocene interacting with phenols. Linear correlation coefficient 0.9855.

The least symmetrical, as far as relative masses of the groups attached to CO, is the carboxaldehydeferrocene which shows the least effect upon the C=O stretching frequencies when the adducts are formed, but similar effects upon the O–H stretching frequencies of the phenols. Using Drago's equations for the enthalpies of interaction of phenol with oxygen and nitrogen donors

$$- \Delta H = 0.0103 \, \Delta\nu_{OH} + 3.08$$

and Purcell's equations (Purcell *et al.* 1969, Purcell and Sherry 1970) for the enthalpies of the interaction of oxygen and nitrogen bases with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 2,2,2-trifluoroethanol (TFE),

$$-\Delta H_{(HFIP)} = 0.0115 \times \Delta\nu_{OH} + 3.6$$

$$-\Delta H_{(TFE)} = 0.0121 \times \Delta\nu_{OH} + 2.7$$

we calculate the enthalpies shown in Table 4. Included in Table 4 are the enthalpies of *N,N*-dimethylacetamide and ethyl acetate for comparison.

With this limited data we could calculate the Drago E_B and C_B parameters for the bases from the Drago equation (Drago *et al.* 1971).

$$- \Delta H = E_B E_A + C_B C_A$$

Drago (1973, 1980) suggests that for any new acid or base four or more enthalpies with as wide a range of C_A/E_A values of the acids will give the best results. The acids used in this study are all hydrogen bonding acids having similar C_A/E_A values (phenol 0.097, HFIP 0.105 and TFE 0.116). Graphs of E_B versus C_B for the substituted ferrocenes show that the three lines for the acids are nearly parallel (for all the substituted ferrocenes). This is a common phenomenon when the C_A/E_A of the

Table 4. Enthalpies of substituted ferrocenes with phenol, HFIP and TFE.

Base	$-\Delta H$ (kcal mol^{-1})		
	Phenol	HFIP	TFE
Benzoylferrocene	5.9	7.3	5.7
Acetylferrocene	6.0	7.9	5.6
Carboxaldehydeferrocene	5.7	7.5	5.3
N,N-dimethylacetamide	6.8	8.5	6.4
Ethylacetate	4.8	6.5	4.4

acids used are similar and the calculated E_B and C_B parameters using such data may be inaccurate.

From the data in Table 4, we can see that all three substituted ferrocenes have similar enthalpies with hydrogen bonding acids, but there are some changes in the order of strengths with each acid. Comparing the enthalpies of the substituted ferrocenes with N,N-dimethylacetamide (DMA) we note that DMA is a stronger base with all three acids. The ethylacetate data indicates|that it is a weaker base with each acid. Using the $\Delta\nu_{OH}$ values obtained by Wettermark *et al.* (1973) and comparing them with the $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ values obtained in this work, we find that $\Delta\nu_{OH}$ (DMA) is linearly related to $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ for the substituted ferrocenes interacting with phenols. Again, the fit is better for the benzoyl derivative than for the other two substituted ferrocenes ($\Delta\nu_{OH}$ vs $\Delta\nu_{CO}$ for benzoyl, linear correlation coefficient 0.9890, for carboxaldehyde 0.9848, for acetyl 0.9879). This encourages us to believe that the data is good and that a study of these ferrocenes with an acid of very different C_A/E_A ratio would lead to the incorporation of substituted ferrocenes into the Drago classification of acids and bases. Unfortunately, acids with larger C_A/E_A ratios than 0.1 can lead to specific reactions or oxidation to ferricinium ion (such as I_2 $C_A/E_A = 1$).

Conclusion

In conclusion, we have shown the similarity of the substituted ferrocenes to oxygen donors of simple organic compounds. Qualitatively, the most symmetrical substituted ferrocene, benzoyl, appears to give better fits to the linear relationships of $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ to the Hammett constant σ.

The present data is insufficient to give accurate values of Drago's E_B and C_B parameters; the interaction with an acid having a widely different C_A/E_A value would need to be determined to give accurate values of E_B and C_B. The present data does fit quite well with the data previously obtained for N,N-dimethylacetamide.

It will be interesting to study substituted benzoylferrocenes* to measure the electronic effects on the basicity of the carbonyl group. It will also be interesting to study substituted ferrocenes having groups with potential nitrogen or sulphur donors.

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*   Referees suggestion.

References

Drago, R.S. (1973) Quantitative evaluation and prediction of donor-acceptor interactions, *Structure and Bonding* **15**: 73-139.

Drago, R.S. (1980) The interpretation of reactivity in chemical and biological systems with the E and C model, *Co-ord. Chem. Rev.* **33**: 251-277.

Drago, R.S. and **Epley, T.D.** (1967) Calorimetric studies of some hydrogen bonding adducts, *J. Am. chem. Soc.* **89**: 5770-5773.

Drago, R.S. and **Epley, T.D.** (1969) Enthalpies of hydrogen bonding and changes in $\Delta\nu_{OH}$ for a series of adducts with substituted phenols, *J. Am. chem. Soc.* **91**: 2883-2890.

Drago, R.S. and **Vogel, G.C.** (1970) Hydrogen bonding of sulphur donors with various phenols, *J. Am. chem. Soc.* **92**: 5347-5341.

Drago, R.S., Bolles, T.F. and **Brown, D.G.** (1968) The linear $\Delta H - \bar{\nu}_{C=O}$ relation of ethyl acetate adducts and its significance for donor acceptor interactions, *J. Am chem soc.* **90**: 5706-5712.

Drago, R.S., Needham, T.E. and **Vogel, G.C.** (1971) A four parameter equation for predicting enthalpies of adduct formation, *J. Am. chem. Soc.* **93**: 6014-6024.

Fisher, K.J. and **Ezeani, C.E.** (1983) Acid base studies of some silylamines $RNHSiMe_3$, *Polyhedron* **2**: 393-395.

Purcell, K.F. and **Sherry, A.D.** (1970) Linear enthalpy-spectral shift correlations for 2,2,2-trifluoroethanol, *J. phys. Chem.* **74**: 3535-3543.

Purcell, K.F., Brunk, S.D. and **Stikeleather, J.A.** (1969) Linear enthalpy-spectral shift correlations for 1,1,1,3,3,3-hexafluoro-2-propanol, *J. Am. chem. Soc.* **91**: 4019-4027.

Wettermark, G., Stymme, B. and **Stymme, H.** (1973) Substituent effects in the thermodynamics of hydrogen bonding as obtained by infrared spectrometry, *J. Am. chem. Soc.* **95**: 3490-3494.

دراسة بالأشعة تحت الحمراء على التفاعل التبادلي بين الفينول والفيروسينات المستبدلة

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تمت دراسة التفاعل التبادلي بين الفينول وكل من أستيل فيروسين وبنزويل فيروسين بواسطة مطياف الأشعة تحت الحمراء فاتضح أن التفاعل الحمضي – القاعدى مقاسا بالتغير الحادث فى ذبذبة تمدد كل من الرابطة O–H والرابطة C=O له علاقة بثابت هامت للفينول. هذا التغير فى الذبذبات لا يكون بالضرورة متصلاً اتصالاً خطيا عندما تكون المجموعات المتصله بـ C=O مختلفة اختلافاً واضحا فى خواصها الإلكترونيه وكتلتها .

حرارات التفاعل المحسوبة لهذه التفاعلات وحساب معامل دراجو E و C لأستيل فيروسين تبين أن هنالك حاجة لإجراء قياسات حرارية أو دراسات لأحماض أكثر تنوعاً .