The Infra-red Spectra of Chelate Compounds. Part I. Systems of Keto–Enol Type.

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The carbonyl frequencies of aldehydes and ketones involved in conjugate chelation are shown to be linearly related to the double-bond character of the enol or ring double bond. The carbonyl frequencies of chelated esters and acids show a similar relationship.

INFRA-RED studies on keto–enol systems indicate that the grouping R·CO·CH:CR·OH is capable of forming a resonance-stabilised intramolecular hydrogen bond of considerable strength. This results in a very large shift of the carbonyl absorptions, whereas normal hydrogen bonding rarely produces shifts of more than 10 cm.$^{-1}$ (Grove and Willis, *J.*, 1951, 877). Observations on the extent of this carbonyl shift offer the best means of studying the strength of the hydrogen bond in such compounds, as the hydroxyl-group absorptions, which are also affected, are usually too broad and shallow for precise measurement.

This " conjugate chelation " was first observed by Rasmussen, Tunnicliffe, and Brattain (*J. Amer. Chem. Soc.*, 1949, **71**, 1068, 1073), in acetylacetone and in acetoacetic ester; it also occurs in enolisable cyclic β-keto-esters (Leonard, Gutowsky, Middleton, and Petersen, *ibid.*, 1952, **74**, 4070). Park, Brown, and Lacher (*ibid.*, 1953, **75**, 4753) found chelation effects in partially fluorinated β-diketones and showed that the carbonyl frequencies revert to normal values when enolisation is precluded by substitution of the central active methylene group.

A similar effect is found in *ortho*-hydroxy-aromatic aldehydes and ketones in which the unsaturation of the ring plays the part of the enol double bond. Hunsberger (*ibid.*, 1950, **72**, 5626) attributed the low carbonyl frequencies found in such compounds as 2-acetyl-1-hydroxynaphthalene and related aldehydes and esters to conjugate chelation, whilst Flett (*J.*, 1948, 1441) reported earlier that the carbonyl frequencies of 1-hydroxyanthraquinones were abnormally low. More recently, Hunsberger, Ketcham, and Gutowsky (*J. Amer. Chem. Soc.*, 1952, **74**, 4839) obtained evidence of a linear relation within the aromatic series between the frequency shifts shown by any one type of carbonyl group and the double-bond character of the ring bond which plays a part in the chelation.

As a preliminary to work which we are proposing to carry out on the infra-red spectra of metallic chelate compounds we have recently examined a number of keto–enol and related materials, and the results obtained form the subject of this communication.

EXPERIMENTAL

The spectra were obtained with a Perkin–Elmer 21B recording spectrometer, a rock-salt prism being used. Samples were examined in chloroform solution at very high dilutions, a 0·4 mm. cell being used with a similar cell containing the solvent placed in the reference beam to eliminate solvent interference. The results relevant to the discussion are given in Tables 1 and 2, and in all cases the carbonyl absorptions have been assigned on the basis of their being the strongest bands in this spectral region.

DISCUSSION

(a) *Aldehydes and Ketones.*—Hunsberger *et al.* (*loc. cit.*) calculated the carbonyl shifts in the spectra of their chelate compounds by comparison with the frequencies of the original aldehydes and ketones, so that salicylaldehyde, for example, is compared with benzaldehyde and 2-acetyl-1-hydroxynaphthalene with 2-acetylnaphthalene. A similar method, applied to the results given in Table 1, suggests that their linear relation between double-bond strength and carbonyl shift does not hold good for aliphatic compounds with full double-bond character. Thus dibenzoylmethane (1600 cm.$^{-1}$) can fairly be compared with benzylideneacetophenone (1667 cm.$^{-1}$) giving a spectral shift of 67 cm.$^{-1}$, but acetylacetone (1608 cm.$^{-1}$) shows a shift of 90—98 cm.$^{-1}$ when compared with acetylacetonyl acetate (1698 cm.$^{-1}$) or the unchelated enol-form of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (1706 cm.$^{-1}$). Similar wide discrepancies are found with the other compounds listed, and Hunsberger *et al.* (*loc. cit.*) also noted that the value for methyl acetoacetate corresponded to only 80% double-bond character. However, it is by no means certain that this is a proper basis of assessment. Although conjugation of a carbonyl group by an αβ-double bond lowers its frequency by 20—30 cm.$^{-1}$, further conjugation in the γδ-position has only a very small effect, and the frequency thereafter remains essentially constant with further extension of the conjugated chain (Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194). It therefore seems likely that any variations in the original carbonyl frequency due to the influence of groups outside the resonant structure will be largely submerged in the major effects of chelation, and the small initial difference between aldehydic and ketonic groups would also be minimised.

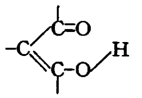
On this basis linearity would be more likely to arise between double-bond character and the actual carbonyl frequencies observed, and the fact that all the values for aliphatic keto-enols listed in Table 1 lie very close to 1600 cm.$^{-1}$ strongly supports this. The four fluoroacetylacetones studied by Park *et al.* (*loc. cit.*) also absorb at this point, probably because the trifluoromethyl group induces enolisation of the adjacent keto-group and is therefore well removed from the carbonyl undergoing chelation. In the four cyclic compounds they examined this is not possible and the chelated carbonyl group is next to the trifluoromethyl group. With such a highly electronegative group some effect upon the carbonyl frequency is not surprising, but even so, the observed range (1637—1621 cm.$^{-1}$) indicates only a relatively small displacement from 1600 cm.$^{-1}$ when compared with the shifts of 60—70 cm.$^{-1}$ found by Haszeldine (*Nature*, 1951, **168**, 1028) in α-fluorinated ketones. We have accordingly plotted the mean of our values and the mean of all the values from salicylaldehyde derivatives directly against double-bond character. The result is shown in Fig. 1 in which the mean values for aldehydes and ketones of intermediate character studied by Hunsberger *et al.* (*loc. cit.*) have been inserted. It will be seen that not only do these points lie reasonably close to the straight line but also that on extrapolation this line cuts the frequency axis at 1708 cm.$^{-1}$. This can be reasonably related to the frequency of the unchelated compound and it compares very favourably with the value of 1706 cm.$^{-1}$ which we have obtained for benzaldehyde and also for the unbonded enol-form of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione.

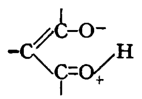
TABLE 1. *Assigned carbonyl frequencies.*

Compound	cm.$^{-1}$	Assignment	Remarks	Compound	cm.$^{-1}$	Assignment	Remarks
Acetylacetone	1724	Keto		2-Cyano-2-methyl*cyclo*hexanone	1721	Keto	*d*
	1608	Enol chelate	*a*				
Benzoylacetone	1724	Keto		Salicylaldehyde	1668	Chelate	*a*
	1600	Enol chelate	*a*	2-Hydroxy-3-methoxybenzaldehyde	1653	,,	*a*
Dibenzoylmethane	1600	,,	*a*				
2-Formyl*cyclo*hexanone	1706	Keto-aldehyde	*a*	2 : 4-Dihydroxybenzaldehyde	1653	,,	*a*
	1596	Enol chelate	*a*				
α-Thenoyltrifluoroacetone	1595	,,	*a*	5-Chloro-2-hydroxybenzaldehyde	1656	,,	*a*
5 : 5-Dimethyl*cyclo*hexane-1 : 3-dione	1733	Keto	*b*	1 : 5-Dihydroxyanthraquinone	1631 1626	,,	*a*
	1706	Free enol	*b*				
	1603	Chelate	*b*	1 : 2 : 5 : 8-Tetrahydroxyanthraquinone	1600	,,	*a*
2-Cyano*cyclo*hexanone	1721	Keto	*c*				

a, Independent of concentration. *b*, Concentration dependent. *c*, C⋮N absorption 2240, 2190 cm.$^{-1}$. *d*, C⋮N absorption 2240 cm.$^{-1}$.

Apparently, the carbonyl frequencies of chelate compounds of this type are determined almost wholly by the character of the double bond involved and this is not unexpected as the length of the double bond will effectively determine the O ··· O distance. The fact that these frequencies are essentially the same in all the aliphatic keto–enol systems studied also indicates that in the resonance between (I) and (II), the contribution of (II) will be the same in all these cases.


(I)


(II)

From the equation derived by Hunsberger *et al.* (*loc. cit.*) this corresponds to about 20—25% in aliphatic keto-enols. As the equilibrium constants of the enols vary widely it also follows that the proportion of this resonant form is not a determining factor in their ionisation and that no relationship is to be expected between their carbonyl frequencies and equilibrium constants. This is in line with the work of Calvin and Wilson (*J. Amer. Chem. Soc.*, 1945, **67**, 2003), which indicated that the equilibrium constants of keto-enols were independent of double-bond character, and it can also be deduced indirectly from the fact that acetylacetone and salicylaldehyde have widely different carbonyl frequencies but very similar K_D values. In the assignment of double-bond character, Pauling's fractional values have been used throughout (Pauling, "The Nature of the Chemical Bond," Oxford University Press). These ignore ionic and Dewar forms, and it is interesting to find that if allowance is made for them and frequencies are plotted against bond orders the agreement is less satisfactory, as resonance of the chelate ring effectively ensures that only the two Kekulé structures are present.

FIG. 1.

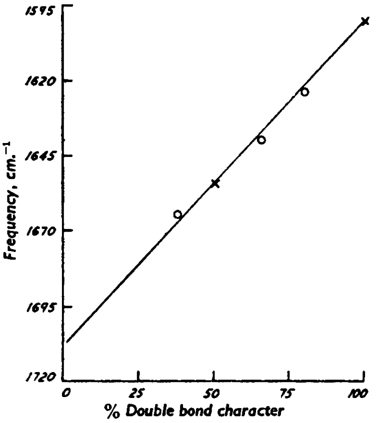
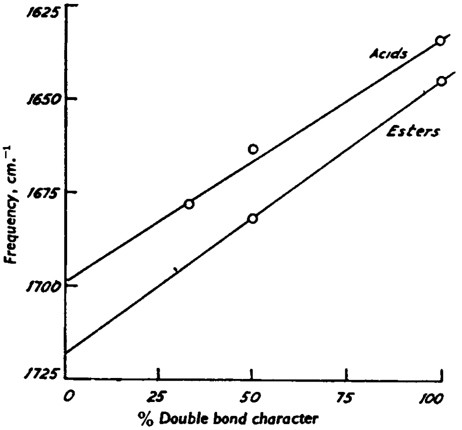


FIG. 2.



These findings do not of course apply directly to the hydroxyanthraquinones examined by Flett (*loc. cit.*) as the introduction of the carbonyl groups directly into the ring results in a substantial degree of bond fixation. Thus the value given in Table 1 for 1 : 5-dihydroxyanthraquinone corresponds to a double-bond strength of about 80% whilst in 1 : 2 : 5 : 8-tetrahydroxyanthraquinone the absorption occurs at 1600 cm.$^{-1}$, suggesting that under the influence of chelation from both sides the ring double bond has become fully stabilised.

It is interesting to find that 5 : 5-dimethyl*cyclo*hexane-1 : 5-dione absorbs at 1603 cm.$^{-1}$ along with the other keto-enols, as in this instance only intermolecular bonding is sterically possible. This band vanishes on dilution; and the 1706 cm.$^{-1}$ band, which we attribute to the unchelated enol, is not linear with concentration but disappears at very high dilutions. At extreme dilutions in non-polar solvents this compound therefore exists only in the diketo-form, which contrasts with its behaviour in the solid state when only chelated enolic carbonyl absorptions are shown. 2-Cyano*cyclo*hexanone and 2-cyano-2-methyl*cyclo*hexanone have been included in Table 1; their spectra confirm the expectation that the hydrogen atom involved in the enolisation of *cyclo*hexanone derivatives must be that which is activated by an attached unsaturated group and cannot, for example, be derived from the 6-position. 2-Cyano*cyclo*hexanone shows evidence of hydroxyl absorption in the 3300 cm.$^{-1}$ region and has two nitrile absorptions at 2242 cm.$^{-1}$ and 2190 cm.$^{-1}$ corresponding to C≡N groups attached to saturated carbon atoms and αβ-unsaturated systems, respectively. 2-Cyano-2-methyl*cyclo*hexanone, on the other hand, is wholly ketonic, shows no hydroxyl absorptions and has only a single C≡N absorption at 2240 cm.$^{-1}$.

(b) *Acids and Esters.*—Acids and esters have not been included in the above discussion as the introduction of a second oxygen atom directly on to the carbonyl group taking part in the resonance can be expected to have a considerably greater influence on its frequency and on the contribution of the resonant form (II) than would result from conjugation or from the alteration of substituents on an aromatic ring. The data available on these compounds are very much limited but it will be seen from Table 2 that the aliphatic esters again show a constant frequency of 1645 cm.$^{-1}$. Leonard *et al.* (*loc. cit.*) reported values between 1653 cm.$^{-1}$ and 1660 cm.$^{-1}$ for six chelated esters of *cyclo*hexanone but as one of these is ethyl 2-oxo*cyclo*hexane-1-carboxylate, for which our value is 1645 cm.$^{-1}$, it is possible that this difference is instrumental and not real. On plotting of the value given in Table 2 against double-bond character (Fig. 2), a straight line is obtained which cuts the frequency axis at 1717 cm.$^{-1}$. This compares well with the value for such unchelated esters as methyl methacrylate (1718 cm.$^{-1}$) and propyl methacrylate (1721 cm.$^{-1}$). Hunsberger's values for the methyl 3-hydroxy-2-naphthoate and for methyl 1-hydroxy-2-naphthoate fall within 2 cm.$^{-1}$ of this line but those for methyl 2-hydroxy-1-naphthoate and methyl 10-hydroxyphenanthrene-9-carboxylate depart from it by about 10 cm.$^{-1}$. A similar plot of the frequencies of the limited number of acids available gives an almost parallel straight line cutting the axis at 1700 cm.$^{-1}$. This also compares well with the range 1692—1700 cm.$^{-1}$ found by Freeman (*J. Amer. Chem. Soc.*, 1953, **75**, 1859), for a series of six alk-2-enecarboxylic acids.

TABLE 2. *Assigned carbonyl frequencies.*

Compound	cm.$^{-1}$	Assignment	Remarks
Ethyl 1-oxotetralin-2-carboxylate	1733	Ester CO	
	1698	Unsaturated keto CO	
	1645	Chelated enol ester	*a*
Ethyl 2-oxo*cyclo*hexane-1-carboxylate	1642	Chelate	*a*
Ethyl 1-methyl-2-oxo*cyclo*hexane-1-carboxylate	1724	Ester CO	
	1712	Keto CO	
Ethyl 2-oxo*cyclo*hexane-1-carboxylate	1724	Keto CO	
	1704	Acid CO	
	1634	Chelate	
Acetoacetic ester	1733	Ester CO	
	1709	Keto CO	
	1645	Chelate	*a*
Methyl salicylate	1668	,,	*a*
Salicylic acid	1661	,,	*a*
2 : 5-Dihydroxybenzoic acid	1669	,,	*a*
2 : 4-Dihydroxybenzoic acid	1653	,,	*a*
3-Hydroxy-2-naphthoic acid	1678	,,	

Despite the limited data available, therefore, it seems very probable that in acids and esters also, the carbonyl frequency is a linear function of the double-bond character but that, owing to the influence of the OH or OR groups, the slope of the line is altered to a lower value than that given by aldehydes and ketones.

As in the case of 2-cyano*cyclo*hexanones, the absence of hydroxyl absorptions and the normal ester carbonyl frequency of ethyl 1-methyl-2-oxo*cyclo*hexane-1-carboxylate when compared with the typical chelate spectrum of the unmethylated derivative confirm that chelation cannot occur when enolisation is precluded by substitution of the active hydrogen atom.

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