502. *Infrared Spectra and Polar Effects. Part VIII.*† *The Frequencies and Stabilities of Olefinic Systems.*

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The C=C stretching frequencies of non-conjugated hydrocarbons are related to the enthalpies of hydrogenation and indirectly to Taft's σ^* reactivity constants of the substituents. A similar relation connects the heats of chlorination of fluorinated olefins with the frequencies but the direction of slope of the resulting line is inverted. The reasons for this are discussed in terms of the factors responsible for the group frequency shifts.

The most useful infrared group frequencies for structural work are those arising from X–H modes and from the stretching motions of multiple bonds. This is because changes of mass in the substituents lead to only very small frequency shifts, whilst the high initial frequencies reduce the incidence of mechanical coupling. For the carbonyl vibration, for example, Halford [1] has shown that the >C=O stretching frequencies are insensitive to mass changes of the substituents for all masses greater than 12, and similar treatments are available for the C≡N [2] and C≡C [3] vibrations. Despite this freedom from mass effects the frequencies of multiple bonds vary widely. The carbonyl absorption, for example, occurs near 1600 cm.$^{-1}$ in compounds such as acetonylacetone [4] but rises as high as 1928 cm.$^{-1}$ in COF_2,[5] and possibly to 2305 cm.$^{-1}$ in $CH_3 \cdot COCl, AlCl_3$.[6] These shifts are due to inductive and mesomeric effects of the substituents [7] together with intramolecular-field effects in special cases.[8] This suggests that the frequency shifts of such vibrations should correlate directly with changes in other physical properties which depend directly upon the same factors. Many such correlations are summarised in ref. 7. They are interesting because of the light they throw on the origins of group-frequency shifts and of the possibility that selected frequency shifts may afford a better measure of the relative magnitudes of polar effects than any other which is yet available.

The commonest examples of relationships between physical properties and group-frequency shifts are those which connect the latter with Hammett's σ reactivity constants,[7] and in some instances the band intensity has been related to the same function.[9] The reactions chosen for such comparisons need to be selected with great care as the kinetics

† Part VII, *J.*, 1957, 4294.

[1] Halford, *J. Chem. Phys.*, 1956, **24**, 830.
[2] Whiffen, *Chem. and Ind.*, 1957, 193.
[3] Lord and Miller, *Appl. Spectroscopy*, 1956, **10**, 115.
[4] Bellamy and Beecher, *J.*, 1954, 4487.
[5] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[6] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 971.
[7] Bellamy, *J.*, 1955, 4221.
[8] Bellamy and Williams, *ibid.*, 1957, 4294.
[9] Steel and Thompson, *Trans. Faraday Soc.*, 1956, **52**, 1451.

of a reaction involving electromeric effects in which the reactant is first polarised by the reagent are not likely to be related to the frequencies of the ground state. However Taft's work [10] on σ* reactivity constants represents an important advance in this respect, enabling Hammett-type relationships to be used in the aliphatic series, and it has recently been shown that σ* values for the appropriate substituents correlate directly with the carbonyl and nitroso-group frequencies of such materials.[11]

Taft and Kreevoy [12] successfully showed that a relationship exists between the enthalpies of hydrogenation of non-conjugated olefins and the σ* values of their substituents. This is subject to limitations in some cases owing to steric factors, and it seemed of interest to see whether the >C=C< frequencies correlated with the same functions, particularly as steric effects would not always have the same effect in the two cases. This study has been extended to a comparison of the frequencies and heats of chlorination of fluorinated olefins which are spectroscopically anomalous in having abnormally high C=C frequencies. The possibility of relations between the frequencies of cyclic olefins and the equilibrium constants for π-complex formation has also been considered.

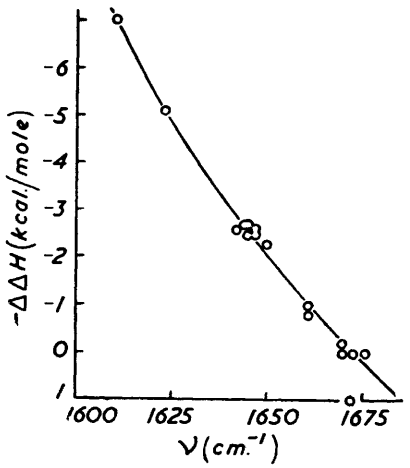


FIG. 1.

Enthalpies of Hydrogenation.—The enthalpies of hydrogenation of a series of olefins are listed at Table 1, together with the corresponding C=C stretching frequencies. Fig. 1 shows that a smooth relation exists. As Taft and Kreevoy [12] have shown that these enthalpies are directly related to σ* values by the expression $\Delta\Delta H = (\Sigma\sigma^*)\rho^* + (\Delta n)h$, this indicates that the frequencies will likewise correlate with the reactivities. Some similarities and differences between these two approaches are noteworthy. In neither case have conjugated compounds been included because the resonance-energy term so introduced is not wholly reflected either in the infrared frequencies or in the σ* values. However, Taft [12] also reported that the enthalpies of *cis*- and vicinally disubstituted ethylenes also failed to correlate with σ* values and he attributed this to steric effects. Although the data are limited, this appears not to be true of the infrared frequencies. The points for both *cis*-but-2-ene and *iso*butene lie on the line of Fig. 1, and even for 2 : 3-dimethylbut-2-ene the discrepancy is only 1 kcal./mole. Further the C=C stretching frequencies of *cis*-isomers are known to be consistently lower than those of the *trans*-forms, in accordance with the observed enthalpies. In cyclic systems however neither the frequencies nor the σ* values are related to the observed enthalpies because the latter now include additional terms involving the change in the geometry of the ring and the numbers of eclipsed CH_2 groups. The frequency for *cyclo*hexene, for example, corresponds to a value on Fig. 1 of −5·0 kcal./mole whereas the observed enthalpy is only −1·0 kcal./mole. For conjugated systems Taft [12] suggests that the degree of divergence from the calculated value measures the extra resonance energy. The divergence for styrene (1630 cm.$^{-1}$) is −5·3 kcal./mole which agrees reasonably well with Taft's value of −4·3.

One point of particular interest arises in connection with the direction of slope of this line. On passing from vinyl chloride to *trans*-but-2-ene, the C=C frequency rises. We suggest that this is due to an increase in the covalency of the multiple bond as the contributions of polar forms such as (I) are reduced. This should increase the stability of

[10] Taft, " Steric Effects in Organic Chemistry," Wiley, New York, 1956.
[11] O'Sullivan and Sadler, *J.*, 1957, 4144.
[12] Taft and Kreevoy, *J. Amer. Chem. Soc.*, 1957, **79**, 4011.

the olefinic bond, and is therefore consistent with the direction of the change of the enthalpy. However *trans*-but-2-ene has an almost wholly covalent bond and therefore

(I) $CH_2{=}\overset{-}{C}H{=}\overset{+}{C}l$ $\qquad$ $F\diagdown \overset{+}{C}{=}CH_2$ $\quad$ (II) $\qquad$ $-F$

represents an end to this process. Any further rise in the C=C frequency can then only come about through the introduction of acetylenic character which would involve contributions from canonical forms such as (II). Hence, continuation of the line of Fig. 1 beyond 1675 cm.$^{-1}$ would lead to a reversal in direction so that any increase in frequency

FIG. 2.

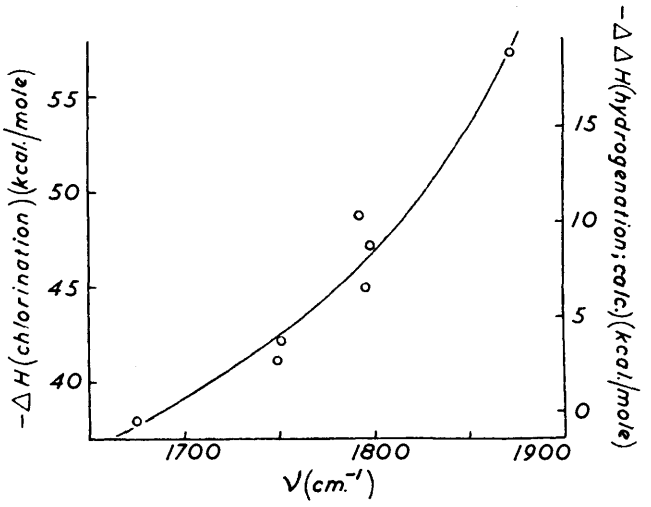
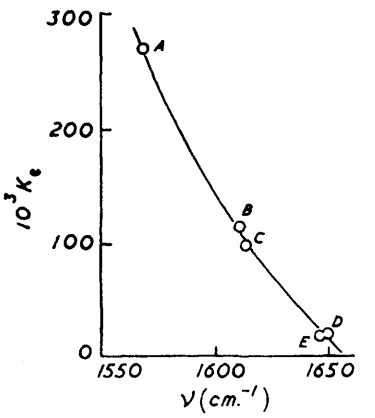


FIG. 3.



would be accompanied by an increase in enthalpy. This possibility has been explored by comparing heats of chlorination of such compounds with their frequencies.

Heats of Chlorination of Fluorinated Olefins.—Reaction of fluoro-olefins with hydrogen does not give the saturated product and hydrogen fluoride is usually displaced, so heats of hydrogenation cannot be measured directly. However, fluoro-olefins are directly

TABLE 1. *Stretching frequencies of the ethylenic bond (cm.$^{-1}$) and enthalpies of hydrogenation ($\Delta\Delta H°$ at 355° K; kcal./mole).*

Compound	ν [a]	$\Delta\Delta H$ [b]	Compound	ν [a]	$\Delta\Delta H$ [b]	Compound	ν [a]	$\Delta\Delta H$ [b]
Ethylene ...	1623	−5·2	3-Methylbut-1-ene	1644	−2·7	*trans*-Hex-2-ene ...	1670	0
Propene ...	1647	−2·5	3 : 3-Dimethylbut-1-ene	1645	−2·7	*iso*Butene	1661	−0·8
But-1-ene	1645	−2·7	*trans*-But-2-ene	1676	0	2 : 3-Dimethylbut-		
Pent-1-ene	1647	−2·6	*cis*-But-2-ene	1661	−1·0	2-ene	1672	+1·0
Hex-1-ene	1642	−2·6	*trans*-Pent-2-ene	1673	0	Vinyl chloride	1610 [c]	−7·0 [d]
Hept-1-ene	1645	−2·5	*trans*-4-Methylpent-2-ene	1670	−0·2	Diethyl fumarate ...	1650 [e]	−2·3 [f]

[a] From Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1, except where stated. [b] From ref. 12 except where other references given; based on *trans*-but-2-ene = −27·6 kcal./mole. [c] Torkington and Thompson, *J.*, 1944, 303. [d] Lacher, Kianpour, Oetting, and Park, *Trans. Faraday Soc.*, 1956, **52**, 1506. Walton and Hughes, *J. Amer. Chem. Soc.*, 1957, **79**, 3985. [f] Turner and Meacher, *ibid.*, p. 4133.

chlorinated, and some thermochemical data are available (see Table 2 and Fig. 2) which, though few, suggest another smooth relation; the enthalpies rise with frequency as suggested above. For comparison we can compute the theoretical enthalpies of hydrogenation of these compounds through the known heats of chlorination and hydrogenation of ethylene, and such values form the right-hand scale of Fig. 2; extrapolation of the line

would intersect the corresponding line of Fig. 1 near 1675 cm.$^{-1}$ and zero enthalpy, this being the frequency of a purely covalent olefinic bond of maximal stability.

TABLE 2. *Heats of chlorination (at 411° K, kcal./mole) and stretching frequencies of the ethylenic bond (cm.$^{-1}$).*

Compound	ΔH [a]	ν	Compound	ΔH [a]	ν
$CH_2{:}CH_2$	−43·6 [b]	1623 [c]	$CF_2{:}CF{\cdot}C_2F_5$	−44·96	1795 [e]
$CF_2{:}CF_2$	−57·32	1872 [d]	$CF_2{:}CCl_2$	−41·07	1749 [g]
$CF_2{:}C(CF_3)_2$	−42·22	1751 [e]	$CF_2{:}CFCl$	−48·81	1792 [h]
$CF_2{:}CF{\cdot}CF_3$	−47·15	1797 [f]	*trans*But-2-ene	−38·4 (calc.)	1676

[a] Lacher, Kianpour, and Park, *J. Phys. Chem.*, 1957, **61**, 584. [b] Konn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 2764. [c] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1. [d] Nielsen, Claasen, and Smith, *J. Chem. Phys.*, 1950, **18**, 812. [e] Brice, Lazerte, Hals, and Petersen, *J. Amer. Chem. Soc.*, 1953, **75**, 698. [f] Nielsen, Claasen, and Smith, *J. Chem. Phys.*, 1952, **20**, 1916. [g] *Idem*, *ibid.*, 1950, **18**, 485. [h] Mann, Aquista, and Plyler, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 1792.

Cyclic Compounds.—The C=C frequencies of cyclic compounds such as *cyclo*pentene, *cyclo*butene, etc., do not obey the relation of Fig. 1, nor does the heat of chlorination of perfluoro*cyclo*butene (−37·4 kcal./mole) correspond to the observed frequency (1785 cm.$^{-1}$). As with the σ^* parameter this is due to the enthalpies' including terms involving the change of the geometry of the ring, but a relation with frequencies might well be found in the special cases of π-complexes in which no such reorganisation occurs. Reactions of olefins with silver ions, for several of which Traynham and Sehnert [14] measured the equilibrium constants, are of this type. Their values (K_e) are plotted in Fig. 3 against the corresponding C=C frequencies (for *A*, *bicyclo*[2 : 2 : 1]heptene; *B*, *cyclo*pentene; *C*, *bicyclo*[2 : 2 : 2]-octene; *D*, *cyclo*heptene; *E*, *cyclo*hexene) given by Lord and Walker.[13] Although only a few points are available a relation of the type expected appears to exist, but it is not a useful one for open-chain systems because the silver ion is known to form a complex as an hydroxylated ion [15] so that steric effects from nearby methyl groups can be considerable. The curve is however of interest from another point of view. Lord and Walker [13] showed that the effect of fusing one ring to an unsaturated one was to increase the strain as judged by the C=C frequency, which fell to a value close to that of the next smaller ring size. A fused *cyclo*pentene system for example absorbs close to *cyclo*butene. It is therefore satisfying to find that K_e for *bicyclo*[2 : 2 : 2]oct-2-ene is not the same as that of *cyclo*hexene but corresponds instead to that of *cyclo*pentene. Similarly, K_e of *bicyclo*[2 : 2 : 1]heptene is much higher than that of *cyclo*pentene and corresponds to the level of activity which might be expected from *cyclo*butene.

Conclusions.—The relations outlined support the view that frequency shifts of carefully selected vibrations can provide quantitative data on the polar properties of substituents. In general these measurements should parallel similar data from reactivities provided the latter do not relate to reactions involving electromeric effects; such comparison might be used to establish when such effects are taking place. The impact of steric effects on frequency shifts and reactivity is also noteworthy. The shifts measure the polarity or triple-bond character in the ground state, and in cyclic systems reflect the degree of strain in the bond itself (they have indeed been so used to assess relative strains in steroid systems [16]). They will be little influenced by steric effects except insofar as the latter changes bond character. But reactivities will clearly be appreciably influenced by steric factors, and the differences may lead to a useful measure of the magnitude of steric factors.

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[13] Lord and Walker, *ibid.*, 1954, **76**, 2518.
[14] Traynham and Sehnert, *ibid.*, 1956, **78**, 4024.
[15] Winstein and Lucas, *ibid.*, 1938, **60**, 836.
[16] Henbest, Meakins, and Wood, *J.*, 1954, 800.