Relation between the Electronegativities of Adjacent Substituents and the Stretching Frequency of the Carbonyl Group

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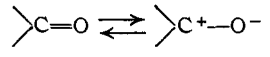
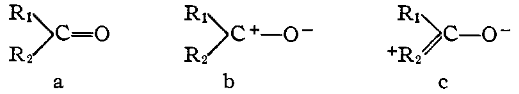
1. Introduction.—Compounds containing the carbonyl group have been the subject of many investigations and a considerable amount of experimental data has been accumulated concerning the vibrational frequencies of the C=O bond. From these data it is possible to draw certain conclusions with regard to the effects of various substituents on the carbonyl frequency. It is well known, for example, that highly electronegative atoms tend to increase the carbonyl frequency and in phosgene ($COCl_2$) the frequency is 1827 cm.$^{-1}$. In formaldehyde (COH_2) the corresponding vibration has a frequency of 1745 cm.$^{-1}$, while in urea the presence of two NH_2 groups results in a lowering of the carbonyl frequency to a value of 1655 cm.$^{-1}$.

Numerous people in the past have pointed out relationships between observed carbonyl frequencies and various structural parameters of the linkage. Recently, Margoshes, *et al.*,[1] have shown a relationship between the bond length and stretching frequency for the carbonyl group. Walsh[2] has also pointed out that the C=O bond lengths in a series of carbonyl compounds is not constant. Comparing this trend in bond lengths with the trend in ionization potentials, Walsh has concluded that the bond length increases with increase in polarity of the C=O bond. This increase in bond length with decrease in ionization potential (and conversely, increase of negative charge on the oxygen atom) occurs because of increased effective size of the oxygen atom or because of increased single bond character according to the scheme

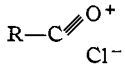


Hartwell, Richards and Thompson[3] have considered the shift in carbonyl frequency in terms of the electronic structures involved. They postulate the existence of three electronic configurations as shown below.

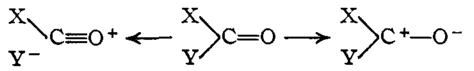


a b c

Pauling[4] and others have suggested that the high carbonyl frequency observed in phosgene and acid chlorides is due to the partial triple bond character introduced into the double bond by the following resonance configuration.



In an actual molecular configuration, therefore, a C=O linkage may assume single or triple bond character according to the scheme



I II

The extent of structures I and II is determined by the electron-attracting or electron-repelling character of X and Y. Thus, if X or Y are strongly electronegative they will tend to pull an electron from the double bond by an induction effect through the carbon atom, and a greater contribution from (I) will result with a consequent increase in the carbonyl frequency. If, on the other hand, X or Y are electron-repelling in character the oxygen atom will gain an electron and the double bond will be weakened due to the contribution of structure (II).

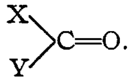
2. Carbonyl Frequencies in Molecules of the Type X·CO·Y.—Since the electronegativity of an atom is a measure of its relative electron-attracting power it would seem logical to expect to observe a relationship between the carbonyl frequency and the electronegativities of atoms X and Y in molecules of the type .

Table I lists the carbonyl frequencies that have been observed for a series of carbonyl-containing compounds. In the third column is listed the arithmetic sum of the electronegativity values of atoms X and Y according to the Gordy scale.[5] It is obvious that the carbonyl frequency and the electronegativity sum are closely related, and this relationship is shown graphically in Fig. 1. Thus there is a linear relationship between the carbonyl frequency and the sum χ_x and χ_y in molecules of the type X·CO·Y.

Table I

Infrared C=O Frequencies of Simple Carbonyl Containing Compounds

Compound	ν(C=O), cm.$^{-1}$	$\chi_x + \chi_y$ (Gordy scale)
A. F·CO·F	1928[a]	7.90
B. F·CO·Cl	1868[a]	6.92
C. F·CO·H	1834[b]	6.08
D. Cl·CO·Cl	1827[a]	5.94
E. H·CO·H	1745[c]	4.26

[a] A. H. Nielsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952). [b] P. A. Staats, H. W. Morgan, J. H. Goldstein, 1954 Columbus Symposium. [c] E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

It would be desirable, of course, to apply this relationship to compounds having a wider variety of substituents X and Y, and indeed experimental data are available for such compounds, where X and Y are no longer single atoms but rather groups of atoms such as $-CH_3$, $-CCl_3$, $-CF_3$, $-CHCl_2$, etc. One is now confronted with the problem of assigning an effective electronegativity value to a group of atoms.

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(1) M. Margoshes, F. Filtwalk, V. A. Fassel and R. E. Rundle, *J. Chem. Phys.*, **22**, 381 (1954).

(2) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 561 (1946).

(3) E. T. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

(4) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

(5) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946). The values used throughout the paper are H = 2.13, C = 2.55, Br = 2.75, Cl = 2.97, O = 3.45 and F = 3.95.

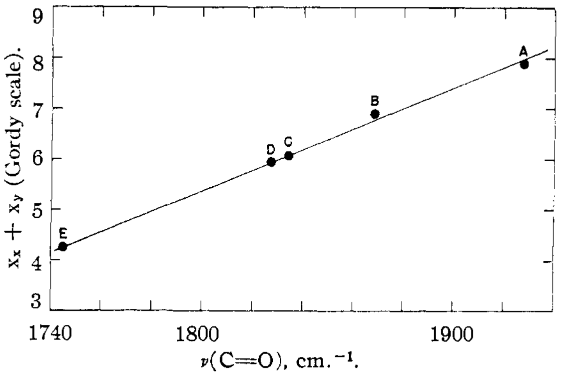
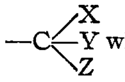


Fig. 1.—Plot of the sum of the electronegativities of substituents X and Y *versus* the observed carbonyl frequencies in compounds of the type X·CO·Y, listed in Table I.

The problem has been approached on a strictly empirical basis for groups of the type  $-\mathrm{C}\begin{smallmatrix}\diagup \mathrm{X}\\ -\mathrm{Y}\\ \diagdown \mathrm{Z}\end{smallmatrix}$ where X, Y and Z are hydrogen or halogen atoms. The object was to find a relationship which would enable one to calculate effective electronegativity values such that the observed carbonyl frequencies and the sum of effective electronegativities would follow the same linear relationship shown in Fig. 1. It has been found that an equation of the form

$$\chi_{eff} = \frac{\chi_C}{2} + \frac{1}{6}(\chi_X + \chi_Y + \chi_Z) \qquad (1)$$

is satisfactory, where χ_C is the electronegativity of carbon (2.55) and $\chi_{X,Y,Z}$ the electronegativities of the various substituents X, Y and Z. The effective electronegativities of typical substituted methyl groups evaluated by means of this equation are listed in Table II.

TABLE II

EFFECTIVE ELECTRONEGATIVITIES OF SUBSTITUTED METHYL GROUPS

Group	$\chi_{eff.}$	Group	$\chi_{eff.}$
$-CH_3$	2.34	$-CH_2Br$	2.44
$-CH_2Cl$	2.48	$-CHBr_2$	2.55
$-CHCl_2$	2.62	$-CBr_3$	2.65
$-CCl_3$	2.76	$-CF_3$	3.20

Table III lists the observed carbonyl frequencies for a group of acid halides and aldehydes along with the electronegativity sum of the substituents. In general there is good agreement between the trend in carbonyl frequency and the electronegativity sum, in spite of the fact that certain frequencies are those observed for the liquid state. It is well known that considerable frequency shifts may occur in going from the vapor to the liquid state, so that the values obtained in different states may not be strictly comparable. Figure 2 shows a plot of the values listed in Table III along with those of Table I. Of the thirteen compounds listed, only CH_3·CO·Cl is in serious disagreement with the proposed relationship. The data listed in Tables I and III have been fitted to an equation of the form $y = a + bx$ by the usual least mean square method and the equation thus obtained is

$$\nu(C{=}O)\ \text{cm.}^{-1} = 1536.5 + 48.85(\chi_X + \chi_Y) \quad (2)$$

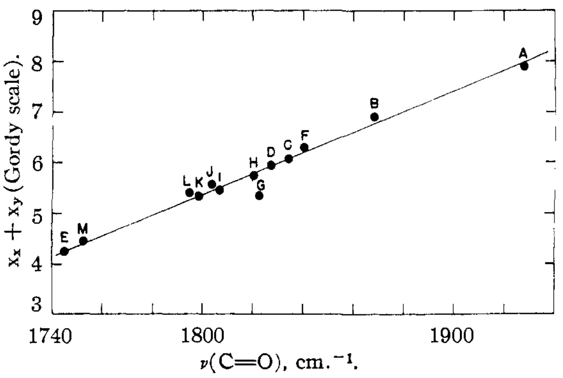


Fig. 2.—Plot of the sum of the electronegativities of substituents X and Y *versus* the observed carbonyl frequencies in the compounds listed in Tables I and III.

TABLE III

OBSERVED CARBONYL FREQUENCIES AND ELECTRONEGATIVITY SUMS FOR SUBSTITUTED ALDEHYDES

	Compound	$\nu(C{=}O)$, cm.$^{-1}$	$\chi_X + \chi_Y$
F.	CH_3·CO·F	1840[b] (liquid)	6.29
G.	CH_3·CO·Cl	1822[a]	5.31
H.	CCl_3·CO·Cl	1820[a]	5.73
I.	CH_2Cl·CO·Cl	1806[c] (liquid)	5.45
J.	$CHCl_2$·CO·Cl	1803[c] (liquid)	5.59
K.	$CHCl_2$·CO·Br	1799[b] (liquid)	5.37
L.	CH_2Br·CO·Cl	1794[b] (liquid)	5.41
M.	CH_3·CO·H	1752[a]	4.47

[a] Hartwell, Richards and Thompson, *J. Chem. Soc.*, 1436 (1948). [b] Seewann-Albert and Kahovev, *Acta Phys. Austriaca*, **1**, 352 (1947). [c] H. C. Cheng, *Z. physik. Chem.*, **B26**, 288 (1934).

The standard deviation between the observed and l.m.s. values for the carbonyl frequencies is 4.27 cm.$^{-1}$.

3. Carbonyl Frequencies in Esters of the Type X–COOR.—Hibben[6] has pointed out that the carbonyl frequency in esters is a function of substitution and depends not only upon the nature of the substituent group but also upon its position in a given homologous series. Consider, for example, the esters represented by the general formula X·CO·OR. The effect of increasing the length of the ester radical, *i.e.*, in going from $-CH_3$ to $-C_2H_5$, $-C_3H_7$, etc., on the carbonyl frequency is negligible. This is at least partly because the hydrocarbon component of the ester radical is in the β-position to the carbonyl carbon. Moreover, if the effective electronegativity values previously listed are sig-

TABLE IV

THE CARBONYL FREQUENCIES IN ESTERS OF THE TYPE X·CO·OR[6]

R	X = H	X = CH_3	X = CH_2Br	X = CH_2Cl	X = $CHCl_2$	X = CCl_3	X = Cl
CH_3	1717	1738	1740	1748	1755	1768	1780
C_2H_5	1715	1736	1738	1747	1750	1763	1772
C_3H_7	1719	1739	1736	1742	1749	1764	1775
C_4H_9	1718	1737	1732	1739	1751	1765	1773
C_5H_{11}	1718	1738	. .	1744	1756	1769	1774
Ave.	1717	1738	1736	1745	1752	1766	1775
χ_X	2.13	2.35	2.44	2.48	2.62	2.76	2.97

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(6) Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publ. Corp., New York, N. Y., 1939, p. 189.

nificant one should not expect any profound changes due to the replacement of a hydrogen atom (χ_H = 2.13) with a methyl group (χ_{CH_3} = 2.35) since they are of comparable values. However, when changes in the substituent at the α-position are made, appreciable changes occur. The observed carbonyl frequencies in Raman spectra of a number of liquid esters are listed in Table IV.

The average carbonyl frequencies for the various esters listed above, plus the value for $CF_3 \cdot COOC_2H_5$ reported by Fuson[7] (ν(C=O) = 1780 cm.$^{-1}$) are plotted in Fig. 3 as a function of the effective electronegativities of group X, which are listed for the most part in Table II. If one assumes that the effective electronegativity of the group -O-R is constant and has the value $\chi_{\text{-O-R}}$ = 1.81, the standard deviation of the observed ester carbonyl frequencies from those predicted on the basis of equation 2 is only ±6.0 cm.$^{-1}$.

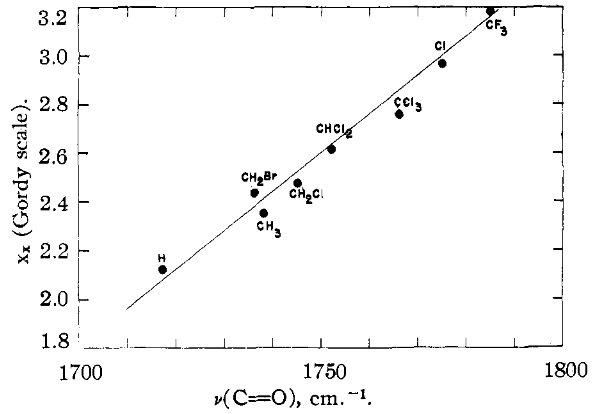

Fig. 3.—Plot of the electronegativity of substituents X *versus* the observed carbonyl frequencies in esters of the type X·CO·OR.

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[7] N. Fuson, M. L. Josien, E. A. Jones and J. R. Lawson, *J. Chem. Phys.*, **20**, 1627 (1952).

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Differential Thermal Analysis of the Thermal Decomposition of Ammonium Nitrate

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The general method of differential thermal analysis (DTA) is well known and has been used extensively in the study of phase changes, dehydrations and general condensation phenomena.[1,2] It does not appear to have been applied, however, to the exothermic decomposition of thermally unstable materials. The results of such an application to the decomposition of ammonium nitrate, reported in the present note, show that the DTA method can give interesting results in this field also.

Experimental.—The DTA apparatus was similar to that described by Vold.[3] A Brown Type 152 preset-program temperature controller, operating a proportioning motor and Variac, was used to cause the wall of the furnace to rise in temperature at a uniform rate of 2° per minute in the range from room temperature to 300°. Absolute and differential temperatures were recorded on a Leeds and Northrup Model S Speedomax Type G two-pen strip-chart X_1–X_2 millivolt recorder. A d.c. microvolt amplifier could be added to the differential temperature circuit, when necessary, by means of appropriate switches. The temperature sensing elements were in all cases single junction, 30 gage, iron–constantan thermocouples, duplex type, insulated with braided nylon and fiber glass. The samples were contained in 10 × 70 mm. Pyrex test-tubes which were suspended from holes in a Transite shelf mounted in the center of a furnace of the type described by Vold.[3] The thermocouples entering the sample test-tubes were inserted into lengths of 3 mm. Pyrex tubing sealed at the bottom.

One-gram samples of reagent grade ammonium nitrate crystals were used and the modifying salt, if any, was added in excess of this. Preliminary experiments showed no change in the DTA curves when the salts were first dried *in vacuo* over P_2O_5. Prior to a run, the apparatus was allowed to equilibrate by maintaining the temperature constant at some value in the range 185–200° for about 30 min. When a steady state had been reached, the differential temperature had in general fallen to some negligible value amounting to about 2% or less of the thermal effects being measured. Duplicate DTA curves agreed to within about 4% or better at all points.

Results.—Typical DTA curves obtained in this work and plotted in the conventional form are shown in Figs. 1 and 2. Numerical data are given in Table I where ΔT_{max} gives the height of the maximum in the differential thermal curve and T gives the temperature at which it occurs. The actual numerical values depend, of course, on the appara-

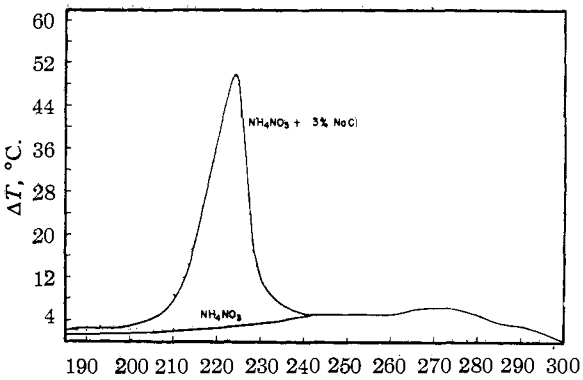

Fig. 1.—Thermal decomposition of ammonium nitrate.

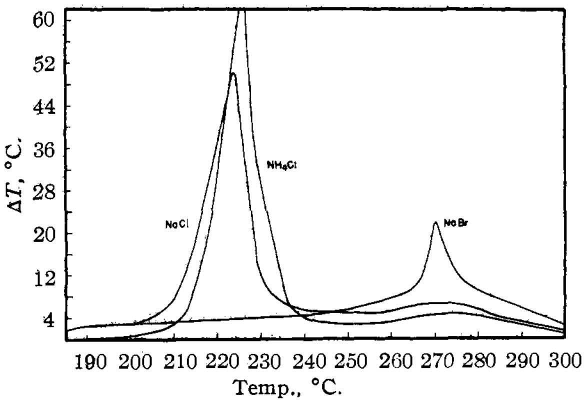

Fig. 2.—Thermal decomposition of ammonium nitrate. Salts shown were added in mole ratio 0.05:1.

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[1] W. J. Smothers, Y. Chiang and A. Wilson, "Bibliography of Differential Thermal Analysis," Research Series Publication No. 21, University of Arkansas, November, 1951.

[2] L. F. Audrieth, J. R. Mills and L. E. Netherton, *J. Phys. Chem.*, **58**, 482 (1954).

[3] M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).