On the whole the present results for the ionic entropies seem to be more consistent with those of Latimer and Jolly than with those of Coulter. The differences are mainly in the choice of free energy values rather than a result of the temperature differences. Although the molar entropy of Ca^{++} in liquid ammonia is expected to be more negative than that of Sr^{++} the difference can hardly be expected to be so great as that (124 e.u.) obtained if Coulter's result for Ca^{++} and the present result for Sr^{++} are both correct. The former result is based upon some e.m.f. measurements by Pleskov (*cf.* Table II) and this comparison supports the view that these e.m.f. measurements are inconsistent with our amalgam partition measurements involving Sr.

For the most part, a detailed consideration of these results is deferred pending the resolution of several uncertainties in the auxiliary data, particularly those relating to the energetics of formation of rubidium amalgam from the elements. However one observation may be made independently of these data. By comparing the equilibrium constant of reaction 1 at 0° with that for the same reaction at 0°, but with H_2O in place of NH_3 as the solvent,[7] we can calculate ΔF^0 for the reaction

$$\frac{1}{z_i}\,M_i^{z_i+}(H_2O) + Na^+(NH_3) \longrightarrow \frac{1}{z_i}\,M_i^{z_i+}(NH_3) + Na^+(H_2O) \quad (7)$$

In this way we obtain

Mi	K	Rb	Cs	Sr
ΔF_7^0	1.55	1.91	2.35	−1.06 kcal./mole

These results are clearly the opposite of what one would expect on the basis of the simple Born charging equation, which predicts that the smaller, more highly charged ion should show the greater preference for the solvent of higher dielectric constant.

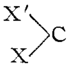
LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM SPECTROSCOPY LABORATORY, THE DOW CHEMICAL COMPANY]

The Donor Characteristics of the Carbonyl Group

BY DENYS COOK

RECEIVED JUNE 6, 1957

The donor characteristics of molecules containing the carbonyl group are examined in terms of the ionization potential (IP), the carbonyl stretching frequency ($\nu_{C=O}$), the value of the fundamental stretching frequency of HCl (ν_{HCl}), dissolved in such solvents, and the value of the acetylenic C–H stretching frequency of C_6H_5CCH (ν_{CH}) in solution in such solvents. Empirical relationships have been found between these quantities for a large number of carbonyl compounds. Donor strengths are discussed in quantitative terms. Modifications of the carbonyl group of  $X'(X)C{=}O$ in terms of the properties of X are examined. The experimental evidence presented suggests that such carbonyl compounds can be divided into two clearly distinguishable classes, (A) where no conjugation between X and C=O exists, and (B) where there is such conjugation.

There have been several studies of the relationship between $\nu_{C=O}$ and carbon–oxygen distance, and other fundamental properties of the carbonyl bond.[1] The important result from such studies is that short bonds have high stretching frequencies and force constants and *vice versa.* The emphasis in such studies has been placed on the electrons in the C=O bond, and little or no attention has been paid to the lone pair electrons.

The carbonyl group consists of a C atom hybridized in its sp^2 state with three planar σ-bonding orbitals, the interbond angle being 120°. The fourth orbital is a p orbital at right angles to the sp^2 hybrids. The carbonyl bond is formed by overlapping one of the sp^2 hybrids of the C atom with a p orbital of the O atom to form the σ-bond, the other p orbital of the O atom forming the π-bond with the C p orbital. On account of the greater electronegativity of the O atom the π electrons will not be equally shared. The O atom $2s^2$ and $2p^2$ have so far not been assigned. A hypothetical model which, however, remains to be confirmed by precise quantum-mechanical calculations, can be set up, wherein these electrons belong to two lone pair orbitals (each doubly filled and non-bonding) in a plane at right angles to the π-bond, with a probable angle of 120° between the lone pair orbitals and the carbon–oxygen σ-bond. Indirect evidence for this arrangement comes from the structure of compounds containing groups capable of hydrogen bonding to the carbonyl group.[2]

The carbonyl group lone pair electrons are responsible for many of the physical properties of such compounds as the carboxylic acids and amides. Thus all simple primary amides, with the exception of formamide, are solids due to intermolecular hydrogen bonds. The corresponding N,N-dialkyl amides, where no such hydrogen bonding can take place, usually have much lower melting points than the unsubstituted amide. The carboxylic acids, except in the gas phase at elevated temperatures, consist of hydrogen bonded dimers or chains. Other carbonyl compounds like ketones, esters and acid halides appear to behave normally because of the lack of an acidic hydrogen atom. Hydrogen bonding has been postulated for aldehydes but its existence seems controversial.

Little is known in quantitative terms of the donor strength of lone pair orbitals. It is the pur-

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(1) See E. M. Layton, R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 138 (1956), for a comprehensive bibliography.

(2) W. G. Schneider, *ibid.*, **23**, 26 (1955).

pose of this paper to show that empirical correlations can be made between such fundamental properties of carbonyl compounds as the IP, $\nu_{C=O}$ and the value of ν_{HCl} for solutions of HCl in such solvents, and ν_{CH} of C_6H_5CCH in solution in carbonyl compounds, enabling interpretation of donor strengths in a quantitative manner.

The Variation of $\nu_{C=O}$ and IP with the Nature of the Substituent.—It is well known that replacement of a hydrogen atom in an aldehyde by an electronegative atom like chlorine raises $\nu_{C=O}$. Fluorine is remarkable in this respect giving, in carbonyl fluoride, one of the highest values known, namely, 1928 cm.$^{-1}$. Replacement by a methyl group will however lower the frequency. Another well known feature of the carbonyl group is the lowering of $\nu_{C=O}$ when the substituent is unsaturated.

Lord and Miller[3] recently have discussed factors affecting $\nu_{C=O}$. They concluded that in the absence of ring strain and hydrogen bonding effects, the inductive effect and conjugation were the determining factors. Kagarise[4] also has shown that for compounds where only the inductive effect is important a quantitative relationship exists between the electronegativity of the substituent X and the value of $\nu_{C=O}$. The substituents considered were alkyl, halogen and halo-alkyl.

When the inductive effect and conjugation are both present it is often difficult to decide which is the major factor. Figure 1 shows how some of these difficulties can be resolved by correlating $\nu_{C=O}$ with IP. Two distinct curves are shown on this graph separated by much more than the experimental error. Curve A, black circles, represents molecules where no conjugation exists between X and C=O. Curve B, open circles, represents molecules where conjugation between X and C=O is, in principle, possible. Data and sources are given in Tables IA and B, respectively. Minor

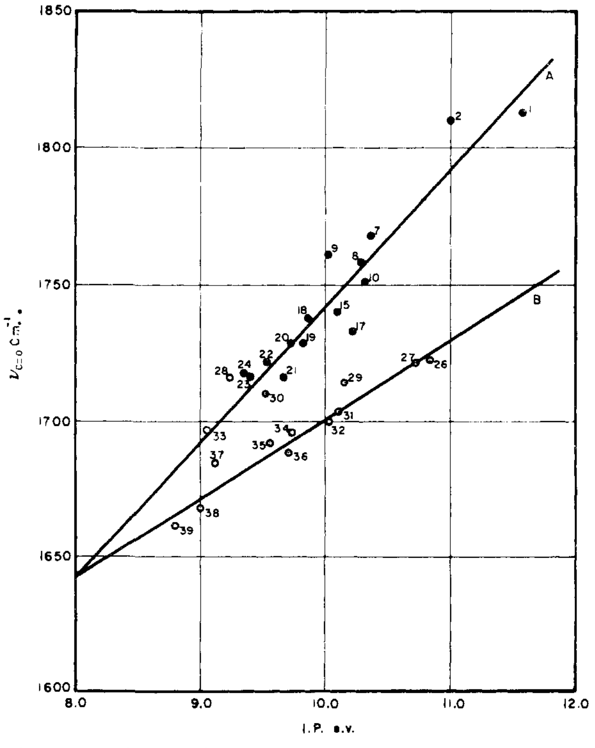

Fig. 1.—Variation of $\nu_{C=O}$ with IP: ●, class A; ○, class B compounds.

TABLE IA

UNCONJUGATED CARBONYL COMPOUNDS

	Compound	$\nu^g_{C=O}$[m]	$\nu_{C=O}$	I.P.[n]	ν_{HCl}	ν_{CH}
1	$COCl_2$	1828[h]	1813	11.57[b]		
2	$CHCl_2COCl$		1810	11.00[c]		3306
3	CH_3COCl	1822[h]	1808		2821	3306
4	$ClCOOCH_3$	1795	1786		2703	3297
5	$CH_3COOC_6H_5$	1793[h]	1780[g]		2663	3287
6	$CCl_3COOC_2H_5$	1786[h]	1770		2747	3301
7	CH_3COOH	1785[h]	1768[l]	10.35[a]		
8	C_2H_5COOH	1787[h]	1758	10.27[b]		
9	n-C_3H_7COOH		1761	10.02[b]		
10	$(CH_3O)_2CO$	1777[h]	1754			3274
11	$HCOOCH_3$	1757[h]	1734		2674	3279
12	CH_3COOCH_3	1774[h]	1751[g]	10.31[d]	2639	3268
13	$(C_2H_5O)_2CO$	1767[h]	1744		2625	3279
14	$(i$-$C_4H_9O)_2CO$		1744			3279
15	$CH_3COOC_2H_5$	1765[h]	1740	10.10[a]	2615	3270
16	n-$C_3H_7COOnC_4H_9$	1752	1735		2603	3266
17	CH_3CHO	1752[h]	1733	10.21[a]	2564	3265
18	C_2H_5CHO	1757[h]	1738[g]	9.86[b]	2597	3268
19	n-C_3H_7CHO	1745	1729	9.81[b]		3263
20	i-C_4H_9CHO	1742	1729	9.72[b]	2610	3265
21	CH_3COCH_3	1742	1717	9.69[a]	2457	3252
22	$CH_3COC_2H_5$	1742[h]	1722	9.54[a]	2505	3252
23	$CH_3COnC_3H_7$	1737[h]	1717	9.39[b]	2488	3247
24	$CH_3COnC_4H_9$	1734	1718	9.38[b]	2497	3247
25	Cyclohexanone	1742[h]	1716		2445	3245

B. CONJUGATED CARBONYL COMPOUNDS

	Compound	$\nu^g_{C=O}$[m]	$\nu_{C=O}$	I.P.[n]	ν_{HCl}	ν_{CH}
26	$HCONH_2$	1740	1722	10.84[a]		
27	$CH_2CHCOOH$		1721	10.70[b]		
28	$CH_3COCOCH_3$	1739 1724	1717	9.25[a]	2668	3279
29	CH_3CONH_2		1714[j]	10.16[d]		
30	C_6H_5CHO	1725[h]	1710[g]	9.51[a]	2597	3279
31	CH_2CHCHO	1733 1714	1704	10.10[a]		3274
32	$CH_3CONHCH_3$	1718[k]	1700[k]	10.01[d]		
33	$(CH_3)_2CCHCOCH_3$	1715	1697	9.05[a]		3246
34	$CH_3CHCHCHO$	1715[h]	1696	9.73[a]		3253
35	$CH_3COC_6H_5$	1707[h]	1692[g]	9.57[b]	2519	3257
36	$CH_2CHCOCH_3$		1689	9.71[b]		3257
37	$HCON(CH_3)_2$		1684	9.11[a,e]		3209
38	$C_6H_5COC_6H_5$		1668[g]	9.00[f]		
39	$CH_3CON(CH_3)_2$	1689	1662	8.80[a]		3215
40	$CH_3CON(C_2H_5)_2$	1678	1649			3203
41	$CH_3CON(nC_4H_9)_2$		1647			3205

[a] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). Also private communication. [b] J. D. Morrison and A. J. Nicholson, *ibid.*, **20**, 1021 (1952). [c] These measurements were made by Dr. W. C. Steele of this Laboratory. [d] K. Higasi, I. Omura and H. Baba, *Nature*, **178**, 652 (1956). [e] I. Omura, K. Higasi and H. Baba, *Bull. Chem. Soc. Japan*, **29**, 502, 504, 521 (1956). [f] Private communication, Dr. K. U. Ingold, Ottawa. [g] G. M. Barrow, *J. Chem. Phys.*, **21**, 1008 (1952). [h] E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948). [i] J. C. Evans, *J. Chem. Phys.*, **22**, 1228 (1954). [j] M. Davies and H. E. Hallam, *Trans. Faraday Soc.*, **47**, 1170 (1947). [k] T. Miyazawa, T. Shimanouchi and S. I. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956). [l] M. Davies and G. B. B. M. Sutherland, *ibid.*, **6**, 755 (1938). [m] All ν are expressed in cm.$^{-1}$. Those without a reference were determined in this Laboratory. To avoid confusion in terminology, $\nu^g_{C=O}$ refers to gas phase values, $\nu_{C=O}$ to dilute (generally 0.01 *M*) solutions in CCl_4. [n] IP are in electron volts. Those with ref. *a* are photoionization data which are compatible with spectroscopic data. All others are electron impact data and have been decreased by 0.2 e.v. This is an arbitrary figure, but makes them more consistent with photoionization data. See ref. *a*.

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(3) R. C. Lord and F. A. Miller, *Appl. Spec.*, **10**, 115 (1956).

(4) R. E. Kagarise, THIS JOURNAL, **77**, 1377 (1955).

uncertainties in the values of IP account for the small scatter. Some anomalies are present in Fig. 1, such as points 28, 30 and 33, which will be discussed in a later section, but on the whole Fig. 1 represents a satisfactory separation of the two classes discussed above.

The following equations have been derived from the data shown in Fig. 1, using the methods of least squares, but omitting points 28, 30 and 33 from the computations.

$$\text{Curve A} \quad \nu_{C=O} = 49.35(\text{IP}) + 1249 \qquad (1A)$$

$$\text{Curve B} \quad \nu_{C=O} = 29.20(\text{IP}) + 1409 \qquad (1B)$$

The values of $\nu_{C=O}$ were obtained using dilute, about 0.01 *M*, solutions of the carbonyl compound in CCl_4. Similar curves were obtained when gas phase stretching frequencies $\nu^g_{C=O}$ were used, and are not shown. Curves obtained using $\nu_{C=O}$ values for the pure liquid phase showed a much larger scatter due to secondary interactions of the carbonyl group. The use of very dilute solutions eliminates the effects of secondary interactions. In this category are included the effects of dimerization of the carboxylic acids and of hydrogen bonding in some amides.

The significance of the correlation presented in Fig. 1 will be discussed more fully later. It is sufficient at this stage to stress that as X changes, both the double bond electrons and the lone pair electrons show modifications which are inter-related.

Interaction of HCl and C_6H_5CCH with Carbonyl Compounds.—In carbonyl compounds the ionization potential is generally thought to be a measure of the energy required to remove one of the nonbonding lone pair electrons. It follows that high IP are associated with tightly bound electrons, and conversely, a low IP means that such electrons are loosely bound. For various donor–acceptor interactions with different molecules it has been shown that there is an inverse relation between the IP of the donor molecule and the strength of the interaction with a constant acceptor.[5,6] Since, as was shown in the last section, different substituents on the carbonyl group modify the IP, it is of interest to inquire if the IP can be used as a measure of the donor strength of such compounds.

A reliable indication of the donor strength of a molecule is the extent to which the fundamental stretching frequency of HCl, ν_{HCl}, dissolved in such compounds is altered from its value in an inert solvent where no specific interaction takes place. Some measurements have been reported by Gordy and co-workers,[7] for carbonyl compounds. They reported values of ν_{HCl} for solutions of the acid in pure solvents. This technique has now been used to evaluate ν_{HCl} for many more carbonyl compounds and a refinement, suggested by work on solutions of HCl in alkyl benzenes[6] has been employed. This consists in diluting the carbonyl compound in CCl_4 to about 10% by volume, and measuring ν_{HCl} for a dilute solution of HCl in such a mixture. ν_{HCl} referred to hereafter will be understood to apply to such a mixture. This has the advantage of avoiding effects due to secondary interactions. These are probably of the type $X'XC{=}O\cdots HCl\cdots O{=}CXX'$ which would give lower values of $\nu_{C=O}$ than the primary interaction $X'XC{=}O\cdots HCl$. The data obtained are shown in Tables IA and IB.

The variation of ν_{HCl} with the IP of the carbonyl compound in which the HCl was dissolved is plotted in Fig. 2. The curve is defined by the linear equation 2

$$\nu_{HCl} = 179.43\ \text{IP} + 807 \qquad (2)$$

There is rather a large amount of scatter on this curve, and it was not possible to include all the compounds in this correlation. Some of the unsaturated compounds, for example, reacted chemically by the addition of HCl.

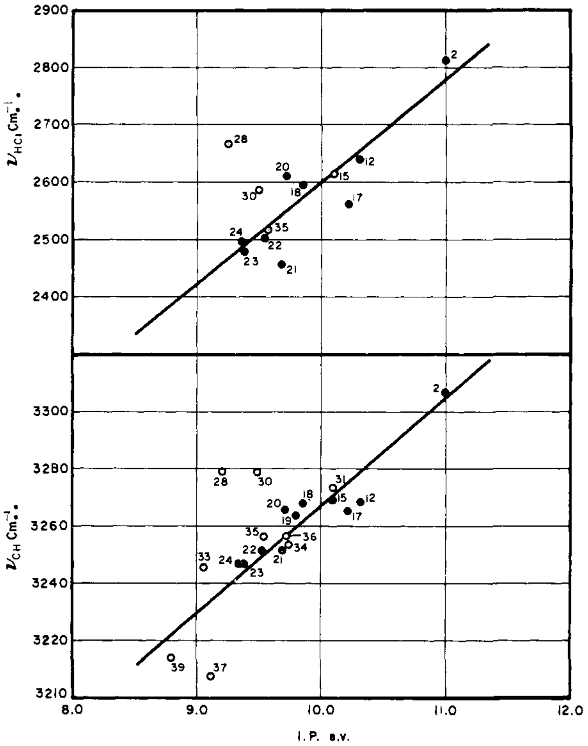

Fig. 2.—(Upper) Variation of ν_{HCl} with IP. Convention as in Fig. 1.

Fig. 3.—(Lower) Variation of ν_{CH} with IP. Convention as in Fig. 1.

Besides this defect of reactivity, the use of HCl to determine donor strengths suffers another serious limitation. In common with many hydrogen bonds between electronegative atoms the resultant infrared band is very broad. The precise measurement of its frequency is a matter of some difficulty. This difficulty has been circumvented by the use of phenylacetylene as the acceptor molecule, at the same time removing some of the objections referred to in the previous paragraph. With phenylacetylene the acetylenic C–H stretching frequency ν_{CH} is perturbed in its interaction with donor groups. This technique has two advantages. Firstly, the resulting perturbed band is still very

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(5) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(6) D. Cook, *ibid.*, **25**, 788 (1956).

(7) W. Gordy, *ibid.*, **7**, 93 (1939); **9**, 215 (1941); W. Gordy and P. C. Martin, *ibid.*, **7**, 99 (1939); W. Gordy and S. C. Stanford, *ibid.*, **8**, 170 (1940); **9**, 204 (1941).

sharp, permitting more accurate measurement of its frequency. Secondly, since phenylacetylene is a liquid it is easier to make up mixtures of known composition. Although the band appears in a region of the spectrum affording slightly lower resolution it is felt that this is outweighed by the advantages of a much sharper band. Gordy and co-workers also used CH_3OD (ν_{OD}) and D_2O (ν_{OD})[7] to determine donor strengths, but these two compounds suffer from the same limitation as HCl in respect of band width.

As was expected, a plot of ν_{CH} against IP shows a reduced scatter, compared to the ν_{HCl} against IP plot, due to the greater precision in the measurement of ν_{CH}. This is shown in Fig. 3. In addition it has been possible to include many more compounds in the latter figure. The data in this figure (also listed in Tables IA and B) have been fitted to the equation

$$\nu_{CH} = 36.54(IP) + 2902 \tag{3}$$

Complete equivalence of the two acceptors HCl and C_6H_5CCH is demonstrated in Fig. 4, where apart from some scatter due to the uncertainty in measuring ν_{HCl} a good straight line results. The curve in Fig. 4 is represented by the equation

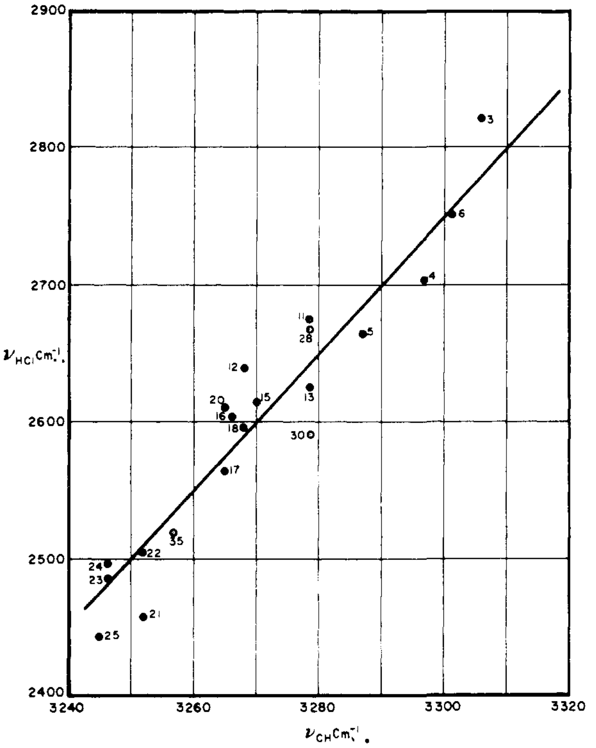


Fig. 4.—Variation of ν_{HCl} with ν_{CH}. Convention as in Fig. 1.

$$\nu_{HCl} = 5.012\ \nu_{CH} - 13{,}789 \tag{4}$$

and was fitted by the method of least squares. Gordy and co-workers also showed by linear relationships the equivalence of using CH_3OD, D_2O, and HCl.[7] Hence all the four acceptor molecules are equivalent in that they all determine donor strengths but with varying degrees of precision.

Equations 2 and 3 provide the kind of relationship that has been sought between ν_{HCl} or ν_{CH}, both experimentally determinable quantities related to the donor strength of the carbonyl group, and the IP which is a fundamental property of the lone pair electrons in the carbonyl group.

To complete this section two further relationships should be noted. These are illustrated in Figs. 5 and 6, and show, respectively, the variation of $\nu_{C=O}$ with ν_{HCl}, and $\nu_{C=O}$ with ν_{CH}. These graphs are similar in many respects to Fig. 1, in that compounds of class A fall on one curve, and those of class B fall on another distinctly separate curve. Figure 6, where C_6H_5CCH is used, has a much larger number of points than Fig. 5 (HCl) for reasons stated earlier. The curves in Fig. 5 have been fitted to the equations

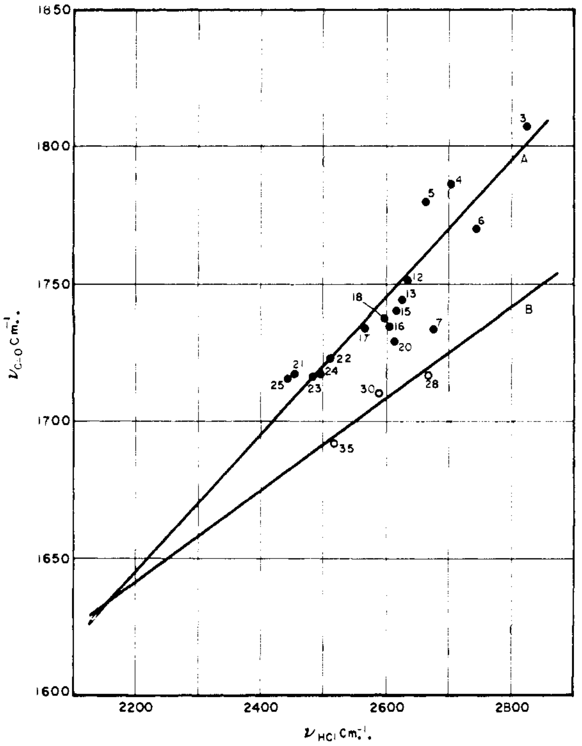


Fig. 5.—Variation of $\nu_{C=O}$ with ν_{HCl}. Convention as in Fig. 1.

$$\text{Curve A} \quad \nu_{C=O} = 0.250\nu_{HCl} + 1095 \tag{5A}$$
$$\text{Curve B} \quad \nu_{C=O} = 0.157\nu_{HCl} + 1300 \tag{5B}$$

and those in Fig. 6 to the equations

$$\text{Curve A} \quad \nu_{C=O} = 1.408\nu_{CH} - 2861 \tag{6A}$$
$$\text{Curve B} \quad \nu_{C=O} = 0.843\nu_{CH} - 1052 \tag{6B}$$

Elimination of $\nu_{C=O}$ from equations 1A and 5A, and 1B and 5B leads to two new equations relating ν_{HCl} and IP which are almost indistinguishable from equation 2. Similarly, equations 1A and 6A, and 1B and 6B give two equations virtually identical with equation 4. The internal consistency of the data is thus demonstrated.

Anomalies.—A few anomalies have been observed in these correlations. Mesityl oxide (33) is one of these, which will be discussed later. Benzaldehyde (30) is anomalous in Fig. 1 since there is nothing to hinder conjugation of the phenyl group with the C=O group, and also in Figs. 2 and 3. However in Figs. 5 and 6 it does seem correctly placed. In view of these considerations it seems that the IP may be suspect. This was one of the compounds listed with slightly lower confidence in ref. *a* (see tables). A value of about 10.3 e.v. would seem more suitable, and would bring it into line with other unsaturated aldehydes in Fig. 1.

Diacetyl (28) is also not well placed in Figs. 1, 2 and 3, but fits the appropriate curve in Figs. 5 and 6. Here again, the IP is the common variable, and an adjustment of this value from 9.25 e.v. to about 10.5 e.v. would resolve this anomaly. The photoionization IP however is supported by an electron impact value of 9.54 (ref. *b* see tables) and the question of this anomaly remains unresolved.

Dimethylformamide (37) is moderately well placed in Fig. 1, but is badly out of line in Figs. 3 and 6. In the two latter figures the common variable is ν_{CH}, and an increase in this value from 3209 cm.$^{-1}$ to about 3240 cm.$^{-1}$ would resolve this anomaly. This difference is certainly outside the experimental error, and the observed band at 3209 cm.$^{-1}$ is quite sharp, and there does not seem to be any interference from other bands. No adequate explanation can be offered for this discrepancy.

Discussion

The linear relationship demonstrated between IP and ν_{CH} (or ν_{HCl} if a lower order of accuracy is accepted) strengthens the use of either as an independent measure of the donor strength of carbonyl molecules. It is interpreted as meaning that, in the absence of any other effect due to strain or steric hindrance, the order of decreasing IP in a carbonyl donor should be the order of increasing strength in the interaction of such a carbonyl donor with a constant acceptor. $\nu_{C=O}$ is more difficult to use as a measure of donor strength since the compound must be unambiguously assigned to either class A or B, and in some cases this may not be possible for various reasons.

The equations presented above may also be used to estimate unknown data, particularly ionization potentials (which require an elaborate apparatus for their determination) with a moderate degree of accuracy, using a very simple spectroscopic technique.

A precise quantum-mechanical description of the mechanism of the modification of the C=O group by different substituents would be mathematically intractable. However, a naive description in terms of the inductive effect and conjugation can be attempted.

It has been shown previously that there is a simple quantitative relation between the electronegativity of a substituent atom or group and $\nu_{C=O}$. To satisfy the electron demands of an electronegative substituent inductive displacements take place in the molecule. Thus the C atom in the C=O bond becomes more positive which will result in displacement of the σ- and π-electrons in the double bond toward this C atom. The σ-displacement will not affect $\nu_{C=O}$ much, but will make the O atom more positive thus enabling it to bind the lone pair electrons more tightly. This will raise the IP. The π-displacement results in more equal sharing of the π-electrons, greater overlap, and therefore a shorter C=O bond with a higher $\nu_{C=O}$. The displacement will also raise the IP somewhat due to decreased electron repulsion between the π-electrons and the lone pair electrons.

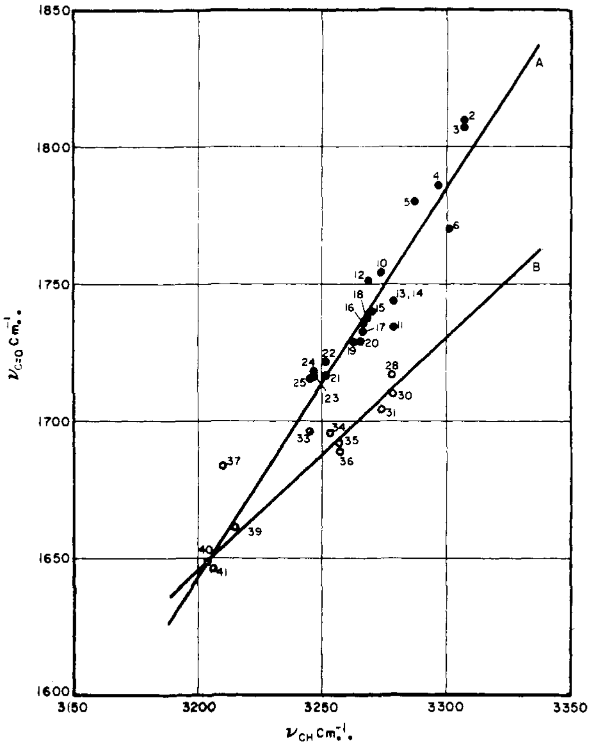


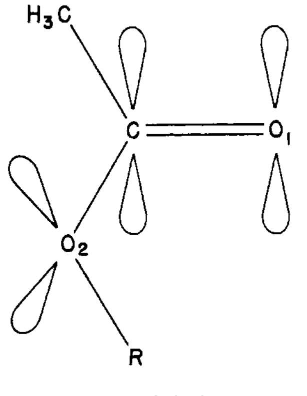
Fig. 6.—Variation of $\nu_{C=O}$ with ν_{CH}. Convention as in Fig. 1.

For compounds where conjugation exists between the substituent and the C=O group, the π-electrons are delocalized and form a molecular orbital extending over four atoms. The overlap between the C and O p orbitals is thus decreased leading to a smaller $\nu_{C=O}$ and a longer C=O bond. The effect on the IP is difficult to assess since the substituent which can conjugate with the C=O group will also exercise some influence on the lone pair electrons through the inductive effect.

Figure 1 can now be examined more closely. The slope of curve A can be interpreted in terms of the inductive effect alone. Thus points at the top right of this curve are for substituents like Cl which are very electronegative (electron withdrawing) while those at the bottom left of the curve are for substituents like alkyl which have the opposite effect (electron release.) Curve B is a little more difficult to interpret, but its downward displacement from curve A suggests that this is the effect of conjugation of the substituent with the C=O group, which lowers $\nu_{C=O}$, while its positive slope, though different from that of curve A is due to the superimposed inductive effect.

These arguments are able to help in the understanding of some of the intramolecular differences in carbonyl compounds. A knowledge of the donor strength of lone pair orbitals enables one to account for a variety of intermolecular effects. Thus the poor solvent power of compounds situated at the top right hand portions of the curves shown above is seen to stem directly from the comparatively inaccessible lone pair electrons. Conversely, the remarkable solvent power of compounds in the lower left hand region of the curves, for example the amides, is due to pronounced, well directed lone pair orbitals which are able to enter into a variety of strong donor–acceptor interactions, hydrogen bonds etc.[8]

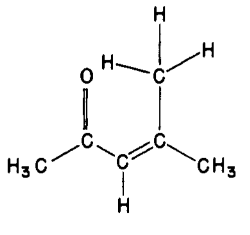
The correlations presented here also can be useful in deciding whether conjugation exists in a molecule or not, provided the required experimental data are known. It will be recalled that the carboxylic acids and their esters all lie on curve A in Figs. 1, 5 and 6, suggesting that there is no conjugation between the C=O group and the ester grouping, or, at least, that it is very small. This suggestion becomes even more plausible on consideration of the spatial arrangement of the ester oxygen atom. It seems certain that this atom has an angular arrangement of its orbitals in a tetrahedral fashion (sp^3), with two of these orbitals containing two non-bonded lone pair electrons (which are, incidentally, much weaker than the sp^2 hybrid lone pair orbitals of the C=O group). This is supported by evidence from structural determinations. The C–O–C angle in the following esters, methyl acetate, 113 ± 4°,[10] methyl chloroformate, 111 ± 4°,[10] monochloromethyl formate, 110 ± 4°,[11] and methyl formate, 112 ± 4°,[10] are all within a few degrees of the tetrahedral angle, and the limits of error in all cases do not preclude this angle. In order for there to be effective conjugation between two groups it is necessary for the overlapping orbitals to lie in the same plane. In the present case where one is a molecular π-orbital (carbonyl electrons) and the other an sp^3 hybrid, it is difficult to see how any effective conjugation can be present as the spatial requirements are not fulfilled. The accompanying drawing illustrates this.



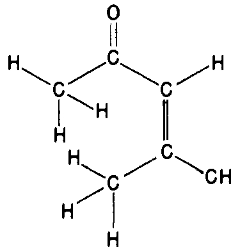
If no conjugation is present between O_2 and C then it is necessary to explain (a) the short O_2C bond length, and (b) the absence of rotation about this bond. The O_2C bond length is about 1.37 Å., much shorter than the C–O bond in an ether. One important difference however between an ether and an ester is the hybridization of the C atom. In an ether this is sp^3, in an ester sp^2 hybridization. It is well known that the covalent radius of a C atom decreases in the series C sp^3 = 0.77 Å. > C sp^2 = 0.67 Å. > C sp = 0.60 Å. This difference between the C sp^3 and C sp^2 covalent radius is of the same order of magnitude as the difference between the ether and ester bond length. The hindrance to rotation seems as if it could be due to the repulsive forces between the ester oxygen lone pair electrons and either the sp^2 lone pair electrons, or the π-electrons of the C=O group. This barrier would be expected to be quite large, and would result in only minor excursions from planarity.

One example of an ester often thought to be conjugated is phenyl acetate. This compound has the remarkably high value of $\nu_{C=O}$ of 1780 cm.$^{-1}$. Although no IP has been reported for this molecule, a value of 10.7 e.v. would be deduced from curve A, Fig. 1. A value of about 12.6 e.v. would be needed if it belonged to curve B, which seems inordinately high for such a complex molecule. Furthermore, though no structure seems to have been determined, it is impossible to construct a model (Stuart–Briegleb type) in which the C=O group is coplanar with the phenyl group. It seems reasonable to conclude that there is no conjugation between the C=O group and the phenoxy group, and that the latter group in phenyl acetate affects the C=O group solely by the inductive effect, and is almost comparable to Cl in this respect.

Some interesting speculations also can be made on the structure of mesityl oxide (33). Although this compound is unsaturated and apparently could have conjugation between the C=C and C=O groups it apparently belongs on curve A. There are good reasons for believing it to be properly placed on this curve, since there is some doubt about the coplanarity of the two double bonds. In the absence of a structural investigation, a molecular model shows that configuration I has some prohibitively close interatomic distances between the β-methyl and the carbonyl oxygen atom, and that configuration II is sterically impossible without some serious distortion of some bond lengths or angles.



I



II

Acceptance of the non-coplanarity of the C=C and C=O groups discounts any effective conjuga-

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[8] Copley and Holley[9] measured the heats of mixing of C_6H_5CCH with dimethylacetamide to be 600 cal./mole; with acetone and methyl acetate it was 250 and 160 cal./mole, respectively. They attributed the large value with the amide to a hydrogen bond between the acetylenic hydrogen and the nitrogen atom. Spectroscopic evidence does not support this contention. In an equimolar mixture of the two compounds ν_{CH} = 3215 cm.$^{-1}$ and $\nu_{C=O}$ = 1642 cm.$^{-1}$. A dilute solution of C_6H_5CCH in CCl_4 gives ν_{CH} = 3311 cm.$^{-1}$. The decrease in $\nu_{C=O}$ in the mixture of the two compounds points to a hydrogen bond to the C=O group. If the hydrogen bond were to the nitrogen a rise in $\nu_{C=O}$ would be expected.

(9) M. J. Copley and C. E. Holley, Jr., THIS JOURNAL, **61**, 1599 (1939).

(10) J. M. O'Gorman, W. Shand, Jr., and V. Schomaker, *ibid.*, **72**, 4222 (1950).

(11) M. Kashima, *Bull. Chem. Soc. Japan*, **25**, 79 (1952).

tion between these two groups and explains why this compound lies on curve A. One is left with the conclusion that since mesityl oxide has a lower IP and $\nu_{C=O}$ than, for example, acetone (21), the $(CH_3)_2C{=}CH$ group must be classed with, but stronger than, CH_3 in its capacity as an electron releasing group.

In conclusion, it should be noted that only compounds with the same functional group, namely, the carbonyl group, can be considered in the present correlations. It would be impossible to include ethers or amines, etc., because the lone pair electrons are in a different configuration. Among themselves, however, ethers or amines, etc., should give the same sort of correlation of donor strength with IP. Lack of experimental data prohibits such a test at the moment.

Experimental

All the spectra were recorded on a double beam spectrometer employing NaCl optics.[12] Immediately after each run the spectrum was calibrated with the 2851 cm.$^{-1}$ and the 1603 cm.$^{-1}$ bands of a thin film of polystyrene. Spectral bands were reproducible to about ± 5 cm.$^{-1}$ at 3,000 cm.$^{-1}$ and to about ± 2 cm.$^{-1}$ at 1700 cm.$^{-1}$. Some runs where a strong solvent band interfered with the measurement were performed differentially using a variable thickness cell.

The great majority of the compounds were Eastman Kodak white label products which were used without further purification. Other reagents were prepared and distilled here.

Hydrochloric acid solutions were prepared by bubbling anhydrous HCl through the appropriate mixture for about 5 minutes. No attempt was made to analyze the mixtures for HCl since its concentration was known to be small. Solutions of C_6H_5CCH in the carbonyl compound were prepared so that the concentration of the former was about 0.5 *M*.

The carbonyl stretching frequencies were measured by making up a solution of the carbonyl compound in CCl_4 to a strength of about 0.01 *M*, and using a cell 0.5 mm. in thickness. Gas phase values of the carbonyl stretching frequencies were measured using a 10 cm. cell at low pressures.

Acknowledgments.—Thanks are due to Professor K. Watanabe for permitting me to see his paper on ionization potentials before publication and for several other unpublished values of IP, to Dr. K. U. Ingold for his unpublished value for benzophenone, and to Dr. W. C. Steele for the measurements he kindly made in these laboratories. The encouragement of Dr. Norman Wright is gratefully acknowledged.

MIDLAND, MICHIGAN

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[12] L. W. Herscher, H. D. Ruhl and N. Wright, *J. Opt. Soc. Amer.*, in press.

[CONTRIBUTION NO. 66 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

2-Methyl-1-propanethiol: Chemical Thermodynamic Properties and Rotational Isomerism[1]

BY D. W. SCOTT, J. P. MCCULLOUGH, J. F. MESSERLY, R. E. PENNINGTON, I. A. HOSSENLOPP, H. L. FINKE AND GUY WADDINGTON

RECEIVED JULY 18, 1957

The chemical thermodynamic properties of 2-methyl-1-propanethiol in the vapor state (0 to 1000°K.) were calculated by methods of statistical mechanics utilizing observed values of the standard entropy, heat capacity and heat of formation. The thermodynamic results are consistent with spectroscopic evidence for a small energy difference between rotational isomers. Experimental studies provided the following information: Values of heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 350°K.) and the vapor (350 to 500°K.); the triple point temperature; the heat of fusion; thermodynamic functions for the solid and liquid (0 to 350°K.); heat of vaporization (321 to 362°K.); second virial coefficient, *B*, in the equation of state, $PV = RT(1 + B/V)$; vapor pressure; and standard heat of formation.

Comprehensive thermodynamic studies of 2-methyl-1-propanethiol (isobutyl mercaptan) were made as part of studies of all seven isomeric thiols and sulfides, $C_4H_{10}S$.[2] The experimental part of this investigation consisted of studies by low temperature calorimetry, vapor-flow calorimetry, comparative ebulliometry and combustion calorimetry. The detailed results are given later in the Experimental section. However, the more pertinent results that are needed for the calculation of thermodynamic properties, as discussed in the next section, are collected in Table I.

Calculation of Thermodynamic Properties

Thermodynamic functions were calculated by standard methods of statistical mechanics. Most of the parameters needed were obtained from available spectroscopic and molecular-structure information; the few remaining were selected to fit the observed values of entropy and heat capacity in Table I. Finally, the calculated thermodynamic functions and the observed value of the heat of formation in Table I were used to calculate the standard heat, standard free energy and common loga-

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES OF 2-METHYL-1-PROPANETHIOL VAPOR

	Entropy, *S*°, cal. deg.$^{-1}$ mole^{-1}			Heat capacity, *Cp*°, cal. deg.$^{-1}$ mole^{-1}	
T, °K.	Obsd.	Calcd.	*T*, °K.	Obsd.	Calcd.
321.31	88.91	88.91	351.20	32.04	32.02
340.07	90.64	90.65	373.20	33.49	33.52
361.65	92.61	92.61	413.20	36.12	36.16
			453.20	38.64	38.63
			500.20	41.33	41.31

$$4C(c,\ \text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$$

$$\Delta Hf^\circ_{298.16}(\text{obsd.}) = -38.48 \pm 0.22 \text{ kcal. mole}^{-1}$$

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[1] This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **79**, 1062 (1957), and earlier publications cited therein.