

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IONIZATION OF ORGANIC ACIDS

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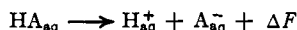
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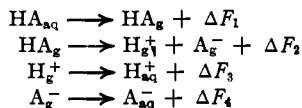
The physical interpretation of the effects of substituent groups upon the acid strength of organic compounds has been the subject of much discussion. Ostwald¹ began the attack on the problem by classifying the various groups as positive or negative according to whether they caused a decrease or an increase in acidity. Since then numerous papers have dealt with the subject in a more quantitative manner, but the treatments have been empirical throughout, in that they have established relationships between the ionization constants of various acids without attempting any numerical correlation of the effect of a particular substituent with the properties of that substituent.

As a result of the recent activity in the measurement of dipole moments, it is natural to suppose that the extent of ionization of an organic acid is affected by the dipoles present in the molecule. This possibility has been considered qualitatively by Wolf,² and Langmuir,³ and, in a more general way, by Briegleb.⁴ The first named author suggested that the acid properties of the carboxyl group are due to the influence of the dipole associated with the carbon-carbonyl oxygen bond. Langmuir pointed out that the dipole associated with the carbon-chlorine bond in mono-chloroacetic acid should facilitate the ionization of the molecule. Briegleb concluded that it is not possible to give a quantitative treatment of the subject, due to the inability of calculating the various free energies of hydration, and of allowing for the effect of association. Although these difficulties would undoubtedly prevent the development of a complete theory, it is possible to give an approximate treatment of the effect of dipole moments upon ionization. Such a treatment may be obtained as follows.

The ionization constant of a weak acid is a measure of the free energy change in the reaction



For purposes of calculation it is simpler to carry out this process in the following manner



¹ W. Ostwald, *J. prakt. Chem.*, **31**, 300 (1885); *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

² K. L. Wolf, *ibid.*, **3B**, 128 (1929).

³ I. Langmuir, *Chem. Rev.*, **6**, 465 (1929).

⁴ G. Briegleb, *Z. physik. Chem.*, **10B**, 205 (1931).

Then

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 = -RT \ln K_a \quad (1)$$

where K_a is the ionization constant of the acid HA and the free energy changes are defined by the various reactions. Of these four free energy terms the second is important for the present purpose. It is, of course, equal to $\Delta E + p\Delta V - T\Delta S$, where the symbols have their usual significance. ΔE , the energy change accompanying the removal of a proton from the neutral HA molecule, is made up of four parts: first, the work of altering the electron distribution from that corresponding to the mainly non-polar binding, present in the neutral molecule, to a distribution corresponding to two ions, H^+ and A^- , situated at a distance equal to their equilibrium separation in the undistorted molecule; second, the work against the Coulomb attraction necessary to remove the H^+ to infinity; third, the change in the polarization energy of the anion due to the removal of H^+ ; and, finally, the work of removal of H^+ from the electric field due to any dipoles in the anion. Of these four contributions to the free energy of ionization, the last is the only one of immediate interest. In general, it is small in comparison with the other energy terms, but it may be brought into prominence, and the difficulties of calculating the other terms may be avoided by comparing the ionization constants of two acids differing mainly in the group moments present in their anions. Let the other member of such a pair be represented by HA' . The corresponding $\Delta F'$ s will be designated by the same subscripts as have been used for HA, but with the addition of primes. Then, if the anions are sufficiently similar, it may be supposed that $\Delta F_2 - \Delta F'_2$ will equal the difference between the work of removal of H^+ from the dipole field of A^- and the work of removal from that of A'^- , say $\epsilon - \epsilon'$. Similarly, if the two compounds are not too different, it may be expected that $\Delta F_1 = \Delta F'_1$ and $\Delta F_4 = \Delta F'_4$. Of course $\Delta F_3 = \Delta F'_3$ for all acids. Since

$$\Delta F' = \Delta F'_1 + \Delta F'_2 + \Delta F'_3 + \Delta F'_4 = -RT \ln K'_a \quad (2)$$

one obtains by subtracting (2) from (1)

$$\Delta F - \Delta F' = \epsilon - \epsilon' = -RT \ln \frac{K_a}{K'_a} \quad (3)$$

The work of removal ϵ is $-e\Phi$, where e is the charge on the hydrogen ion, and Φ is the potential due to the group moments of the anion calculated at the point occupied by the hydrogen nucleus in the undissociated molecule. Similarly, $\epsilon' = -e\Phi'$. By substitution

$$\log \frac{K_a}{K'_a} = \frac{e(\Phi - \Phi')}{2.3kT} \quad (4)$$

The dielectric constant of water, the medium in which the dissociation actually takes place, does not appear in this equation because the energy terms affected by this quantity occur in the free energies of hydration, which have been assumed to cancel. This is not true of some analogous calculations by Bjerrum,⁵ in which the dielectric

⁵ N. Bjerrum, *Z. Physik. Chem.*, **106**, 219 (1923).

constant of water does appear. The latter calculations evaluate the ratio of the first and second ionization constants of some dibasic acids, taking account of the energy necessary to remove the second hydrogen ion from the field of the negative charge left by the first ionization, the whole process being assumed to take place in the solvent. This discrepancy between Bjerrum's work and the present treatment is only apparent, since in his case a cyclic process could not lead to cancellation of the free energies of hydration, due to the difference in charge of the two anions compared (HA^- and A^-). The inclusion of this change in the free energies of hydration involves the introduction of the dielectric constant of water.

It might also be pointed out that the present treatment avoids the difficulty of allowing for the association of the neutral acid molecules in solution, by means of the assumption that the extent of the association of the unsubstituted acid is practically the same as that of the substituted.

Equation (4) will first be applied to the rather extreme case of formic acid and methyl alcohol. It is necessary to assume detailed models of the molecules under discussion: that used for formic acid is shown in Fig. 1,

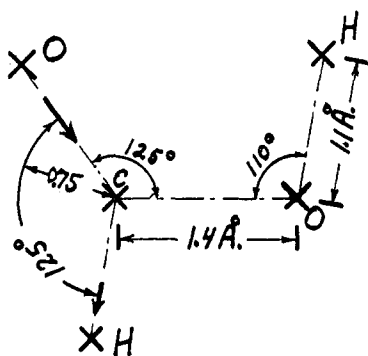


Fig. 1.—Model of formic acid.

together with the necessary dimensions. The potential at the hydrogen nucleus is made up of one contribution from the $\text{C}=\text{O}$ group moment and one from the $\text{C}-\text{H}$ group moment, the potential of a dipole of strength μ being given by the relation

$$\Phi = \frac{\mu}{r^2} \cos \angle (\mu, r) \quad (5)$$

where r is the radius vector from the dipole to the point at which the potential is calculated. The $\text{C}-\text{O}$ group moment is neglected, since it is present with the same

orientation in both molecules. Φ' , the analogous quantity for methyl alcohol, is due to three CH moments. Here, however, it may be supposed that the methyl group can rotate about the $\text{C}-\text{O}$ bond. Formic acid is presumably a plane molecule, since the strong interaction between the OH and CO moments completely prevents rotation at ordinary temperatures.⁶ To take into account the rotation of the methyl group it is necessary to average Φ' over the azimuthal angle about the CO bond.

This averaging is effected as follows: a set of coördinates is so chosen that (1) the X -axis coincides with the axis of rotation in the molecule, and (2) the group moment, whose potential is to be averaged, is contained in the XY plane. Then

$$\begin{aligned} \bar{\Phi} &= \frac{1}{\pi} \int_0^\pi \Phi d\varphi \quad (6) \\ &= \frac{A}{\pi} \int_0^\pi \frac{d\varphi}{(p^2 - q^2 \cos \varphi)^{3/2}} + \frac{B}{\pi} \int_0^\pi \frac{\cos \varphi d\varphi}{(p^2 - q^2 \cos \varphi)^{3/2}} \end{aligned}$$

⁶ L. Meyer, *Z. physik. Chem.*, **8B**, 27 (1930).

where φ is the azimuth about the axis of rotation, and

$$\left. \begin{aligned} A &= \xi(x_H - x_m) - \eta y_m; B = \eta y_H \\ p^2 &= (x_H - x_m)^2 + y_H^2 + y_m^2; q^2 = 2 y_H y_m \end{aligned} \right\} \quad (7)$$

In equation (7) ξ and η are, respectively, the x and y components of the group moment; x_H, y_H the coordinates of the ionizing hydrogen nucleus; and x_m, y_m those of the group moment. Evaluation of the integrals⁷ leads to the expression

$$\bar{\Phi} = \frac{2}{(p^2 + q^2)^{1/2} \pi} \left\{ \frac{1}{p^2 - q^2} \left[A + \frac{Bp^2}{q^2} \right] E - \frac{BK}{q^2} \right\} \quad (8)$$

where K and E are, respectively, the complete elliptic integrals of the first and second kinds for the modulus

$$k = \left(\frac{2q^2}{p^2 + q^2} \right)^{1/2} \quad (9)$$

The values of the group moments used for these calculations, together with the necessary molecular dimensions, have been summarized in Table I. In addition to these, the following values have been used. The angle between the oxygen valence bonds has been assumed to equal 110° , the aliphatic carbon bonds to possess tetrahedral symmetry, the benzene nucleus to be a regular plane hexagon. Group moments have been assumed to lie along the valence bonds and to be situated at a point 0.75 \AA . from the carbon nucleus (0.6 \AA . from the oxygen nucleus in OH). A moment whose positive end is farthest from the carbon nucleus (from the oxygen nucleus in OH) is written + and *vice versa*. The magnitudes of the group moments have been obtained from the resultant moment of the corresponding mono-benzene derivative, as listed by Smyth,¹ with the assumption that $\mu_{CH} = +0.5$. Reasons for the use of these values will be presented in a future article. The group moments of the nitro and cyano groups have been located 0.4 \AA . beyond the N and 0.75 \AA . beyond the C nuclei, respectively.

TABLE I

Group	Internuclear distance, Ångström units	Electric moment $\times 10^{18}$	Group	Internuclear distance, Ångström units	Electric moment $\times 10^{18}$
CH	...	+0.5	CCN	$d_{CC}=1.5$	-3.4
C—O	1.4	...	C—NO ₂	$d_{CN}=1.44$	-3.4
C=O	...	-2.2	C—C _{aliph.}	1.5	0
CF	...	-0.95	C \equiv C	1.2	0
CCl	...	-1.05	C—C _{arom.}	1.4	0
CBr	...	-1.0	OH	1.1	+1.6
CI	...	-0.8			

Application of equations (4) and (8) to formic acid and methyl alcohol leads to a calculated value of the ionization constant of the latter compound of the order of magnitude 10^{-17} . This quantity has not been measured, but it is safe to assume that this calculated value is too high, since smaller ionization constants have been measured. The discrepancy is due to the neglect of the resonance energy of the carboxyl ion, recently pointed out by

⁷ Cf. Bierens de Haan, "Nouvelles Tables d'Intégrales Définies," Leiden, 1867, Table 67, p. 102, equation (3) and (4). Equation 4, as given by de Haan, is incorrect. The correct value for this integral has been used in the present calculations.

⁸ C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, pp. 195 and 203.

Pauling.⁹ According to his estimations, this effect should increase the strength of formic acid to about 10^{13} times that of methyl alcohol. Taking into account both the dipole repulsion and the resonance energy, the expected value for the ionization constant of methyl alcohol is $\sim 10^{-80}$, an entirely reasonable figure. It may be concluded that the acid properties of the carboxyl group are due in part to the substitution of a repelling carbonyl group moment for two attracting CH dipoles, and in part to the resonance energy of the carboxyl ion, the two effects being of approximately the same importance.

A more satisfactory test of the present treatment may be obtained from a study of the substituted acetic, propionic and benzoic acids and the substituted phenols. The calculations are entirely analogous to the previous case, and need not be given in detail. It has seemed best to compare the calculated change in energy of ionization, $(\Delta E - \Delta E')_{\text{calcd.}} = -e(\Phi - \Phi')$, with the experimental values, $(\Delta E - \Delta E')_{\text{obs.}} = 2.3RT \log K_a/K'_a$. These quantities, expressed in kilocalories per mole, are listed in Table II for most of the substituted acids for which data are available and which are amenable to treatment. The list is greatly diminished by the fact that the present method of calculation is limited to molecules in which there is only one effective possibility of rotation between the substituent group moments and the ionizing hydrogen. Further limitations will be mentioned below. Inspection of Table II shows that there is good agreement in some cases and definite disagreement in others. The causes of these discrepancies are, in most cases, apparent.

The first of such departures is found for the poly substituted acetic acids. These deviations must be ascribed to alterations of the magnitudes and directions of the group moments due to the intense interaction of the substituents. The data necessary to show that this is the case are available, if it be assumed that the effects of distortion and induction in di- and trichloroacetic acids are the same as in methylene chloride and in chloroform, respectively. Using the valence angles deduced from the x-ray measurements of Bewilogua¹⁰ and group moments calculated from the molecular moments listed by Smyth,¹¹ together with the assumption that the CH moment equals 0.5×10^{-18} , one obtains the figures listed in the last column of Table II. These are seen to be in good agreement with the experimental values.

Further discrepancies are apparent in the compounds containing nitro groups. These are most probably caused by the use of a single resultant moment for this substituent. Taking the complexity of the nitro group into account would improve the agreement but, in the absence of data

⁹ L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932), and personal communications.

¹⁰ L. Bewilogua, *Physik. Z.*, **32**, 265 (1931).

¹¹ Ref. 8, pp. 192 and 201.

TABLE II

HA	HA'	ΔE - $\Delta E'$ obs. ^a	calcd.	(k cal./mole calcd.)
CH ₂ F ₂ COOH	CH ₃ COOH	2.8	3.5	
CH ₂ ClCOOH		2.6	3.7	
CH ₂ BrCOOH		2.6	3.6	
CH ₂ I ₂ COOH		2.3	3.1	
CH ₂ CNCOOH		3.1	9.2	
CHF ₂ COOH		4.8	6.9	
CHCl ₂ COOH		4.7	7.5	6.2 ^b
CCl ₃ COOH		6.6	11.2	8.7 ^b
CH ₃ C≡CCOOH		2.9	2.7	
CH ₃ CHClCOOH	C ₂ H ₅ COOH	2.8	3.7	
<i>o</i> -C ₆ H ₄ ClOH	C ₆ H ₅ OH	1.2	1.3	
<i>p</i> -C ₆ H ₄ ClOH		0.8	3.5	
<i>o</i> -C ₆ H ₄ NO ₂ OH		3.9	11.0	
<i>m</i> -C ₆ H ₄ NO ₂ OH		2.7	7.4	
<i>p</i> -C ₆ H ₄ NO ₂ OH		3.8	6.6	
<i>m</i> -C ₆ H ₄ F ₂ COOH		0.4	1.9	
<i>o</i> -C ₆ H ₄ ClCOOH	C ₆ H ₅ COOH	1.8	-0.4	0.7 ^c
<i>m</i> -C ₆ H ₄ ClCOOH		0.5	2.1	
<i>p</i> -C ₆ H ₄ ClCOOH		0.2	2.3	
<i>o</i> -C ₆ H ₄ BrCOOH		1.8	-0.6	0.6 ^c
<i>m</i> -C ₆ H ₄ BrCOOH		0.4	2.1	
<i>p</i> -C ₆ H ₄ BrCOOH		(0)	2.1	
<i>o</i> -C ₆ H ₄ I ₂ COOH		1.8	-0.3	0.5 ^c
<i>m</i> -C ₆ H ₄ I ₂ COOH		0.5	1.8	
<i>o</i> -C ₆ H ₄ NO ₂ COOH		2.7	2.3	
<i>m</i> -C ₆ H ₄ NO ₂ COOH	1.0	4.6		
<i>p</i> -C ₆ H ₄ NO ₂ COOH	1.1	4.7		

^a Calculated from ionization constants at 25° listed by H. Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, 1914.

^b Corrected for interaction of group moments.

^c Calculated assuming rotation to be completely frozen out.

indicating the magnitudes of the N=O and C—N moments, it has not seemed worth while to attempt a more detailed calculation for these compounds. The agreement shown by *o*-C₆H₄NO₂COOH is probably fortuitous, the effect of hindered rotation (discussed below) counterbalancing the effect of using a resultant moment for the nitro group.

The most serious discrepancy is shown by the ortho halobenzoic acids, for which compounds the calculations indicate that the substituent halogen should cause a decrease in acid strength. This is undoubtedly due to a hindered rotation of the carboxyl group. If it be assumed that the rotation is entirely frozen, the ionizing hydrogen being as far from the substituent as possible, the figures listed in the last column of Table II are obtained.

Finally, it should be pointed out that there is a pronounced tendency for the calculated values to be higher than the observed. In all probability

this is due to the neglect of the change in polarization energy of the anion upon substitution (the third part of ΔE , p. 3049). This cannot be allowed for numerically, since the electric intensities are so great that polarizabilities calculated from refractive indices no longer have any meaning. It is, however, worth noting that this divergence is roughly proportional to the polarizabilities of the substituent groups.

The only definite discrepancy that has not been accounted for is shown by cyanoacetic acid. Judging from the other results, this departure is too large to be explained by the omission of the polarization energy of the anion. The experimental value for *p*-bromobenzoic acid is enclosed in parentheses because it is of a lower order of accuracy than the other figures.

It has been shown empirically by a number of authors, in particular by Derick,¹² that the change in free energy of ionization upon substitution is an additive property of the nature and relative position of the substituent. This rule is explained by the present treatment as follows. According to the assumptions used above, the change in free energy equals the change in energy of removal of the hydrogen ion. The latter quantity is proportional to the electrostatic potential of the group moment of the substituent, and since the potential is an additive quantity the change in the free energy of ionization must also be additive. As an illustration of this rule, it might be mentioned that $\Delta E - \Delta E'$ for picric acid (compared with phenol) is equal to the energy difference for *p*-C₆H₄NO₂OH plus twice that for *o*-C₆H₄NO₂OH.

Numerous papers have dealt with the effect of removing the substituent along the straight chain of an aliphatic acid. According to equation (5) the effect of the substituent should vary with the inverse square of the distance, provided the angle between the group moment and the radius vector to the ionizing hydrogen remains the same. In general, this will not be the case, and it is this angle which is most important in determining the magnitude of the effect. The large number of rotations, which take place to a more or less limited extent in a straight chain, precludes applying the present calculations to any aliphatic acids except those substituted in the alpha position.

Finally, it is desirable to consider briefly the assumptions underlying equations (4) and (8). First, the cancellation of the free energies of hydration, to within 1-2 k. cal., seems probable upon recalling that these quantities are dependent in part upon the orientation of the water dipoles in the field of the negative charge, if any, and in the field due to the dipoles of the particle; and in part to dispersion attraction. The first effect cannot be altered greatly by substitution since the domain of the —COO⁻ group is not affected. The increase in diameter of the anion occurs in a region relatively

¹² Derick, *THIS JOURNAL*, **33**, 1167 (1911); **34**, 74 (1912); Derick and Kamm, *ibid.*, **39**, 38 (1917); Derick and Hess, *ibid.*, **40**, 537 (1918).

far from the location of the charge and therefore in a region where this effect is least.¹³ The orientation in the dipole field and the dispersion attraction probably differ for the substituted and unsubstituted acids. They should, however, affect by the same amount the free energy of hydration of the anion and that of the undissociated molecule so that they cancel upon adding ΔF_1 to ΔF_4 .

It is necessary to consider in more detail the assumptions made concerning the extent of rotation about valence bonds. It has been assumed that there is no rotation in the carboxyl group, or in the ortho halobenzoic acids, but that in all the other compounds treated the acid group rotates freely with respect to the rest of the molecule. These suppositions may be justified qualitatively as follows. Whether or not rotation takes place depends on the accompanying change in the internal energy of the molecule. This energy is made up of (1) dipole attractions or repulsions, (2) changes in polarization, due to changes in dipole fields, (3) steric repulsions.¹⁴ Only the first of these terms can be calculated, at present; even here the accuracy is probably not very great due to the close approach of the group moments. The direction and extent of the other two terms may at least be estimated, the first from the polarizabilities of the groups between the rotating dipoles, and the second from internuclear distances. Upon applying the calculation of the dipole energy to the carboxyl group, it is found that this term is very large. Since steric hindrance and polarization should be negligible for this group, it is almost certain that rotation is frozen out, as was indicated by Meyer.⁶ In the mono-halo-acetic acids the dipole energy is again large, but here one would expect appreciable change in the polarization energy. The dipole term favors that position of the molecule in which the ionizing hydrogen is as near as possible to the substituent. The polarization energy has the opposite effect. In the configuration corresponding to minimum dipole energy there must be considerable steric hindrance. The net effect cannot be predicted with any certainty, but it seems most probable that rotation is nearly free. In any case the assumption of free rotation is not critical for these compounds, since here Φ does not change greatly upon rotation.

This is not true, however, of the ortho phenols and the ortho benzoic acids where Φ changes sign as φ goes from 0 to π . In both of these classes of compounds there is a relatively small dipole energy tending to hold the ionizing hydrogen near to the substituent. No steric hindrance is to be expected in *o*-C₆H₄ClOH, but the polarization energy, due to the easily deformable aromatic C-C bonds, should be enough to counteract the dipole energy, so that rotation about the C-O bond may be expected to take place.

¹³ T. J. Webb, *THIS JOURNAL*, **48**, 2589 (1926).

¹⁴ The change in dispersion energy is negligible for the compounds under consideration. Cf. H. A. Stuart, *Phys. Rev.*, **38**, 1372 (1931).

The ortho halobenzoic acids differ from the phenols in that the position of minimum dipole energy for the former compounds involves so great a steric hindrance that the configuration becomes extremely improbable. Rather than attempt a discussion based on partially restricted rotation, it has seemed best to include values based on the extreme assumption of no rotation, but with the ionizing hydrogen fixed at the farthest point from the substituent. Interactions between the substituent and the acid group in the meta and para compounds are too slight to affect the rotation.

Extremely interesting information on the gradual loosening of a restricted rotation might be obtained by comparing the ionizations of ortho substituted benzoic acids with that of benzoic acid over as wide a temperature range as possible. Similar studies on phenols might also be of value in this connection, but here it would probably be necessary to go to lower temperatures. From the present discussion it is to be expected that at sufficiently low temperatures the ionization of *o*-C₆H₄ClOH will approach that of phenol, and that at high enough temperatures that of *o*-C₆H₄ClCOOH will approach that of benzoic acid. It is not possible to calculate the temperatures at which these changes should take place; it may be that they are beyond the experimental range. By choosing the substituent groups suitably, however, it should be possible to find compounds in which the free energies of ionization, relative to the unsubstituted acid, change profoundly with the temperature.

Indications of the expected change are definitely shown by the few compounds for which Scudder gives data at more than one temperature. These data are listed in Table III, the ($\Delta E'$)'s being obtained from the ionization constants of benzoic acid at the appropriate temperatures. It is apparent that the strengthening effect of the substituent in the ortho compounds decreases with increasing temperature, while the effect of the substituent in the meta position is essentially independent of the temperature. This is in entire accord with the predictions of the present treatment: in the ortho compounds there is sufficient steric hindrance to hold the ionizing hydrogen in a region where the substituent's group moment repels the H⁺ and so causes an increase in acidity. As the temperature increases the amplitude of oscillation about the bond between the COOH and C₆H₄X groups increases, with the result that the H⁺ spends more and more time in regions of decreased repulsion or even of attraction. At sufficiently high temperatures it is to be expected that *o*-C₆H₄ClCOOH will be weaker than benzoic acid. No such effect is found or expected in the meta acids since in these compounds the steric effects, if any, should be essentially the same as in the unsubstituted acid. The five compounds listed in Table III are by no means enough to establish the present interpretation, but it may be considered that they bring to it definite confirmatory evidence.

TABLE III
 $(\Delta E - \Delta E')_{\text{obs.}}$ K. cal./Mole.

<i>t</i> , °C.	0°	25°	50°	90°
<i>o</i> -C ₆ H ₄ ClCOOH	...	1.8	1.6	1.4
<i>o</i> -C ₆ H ₄ I ₂ COOH	...	1.8	1.6	1.4
<i>o</i> -C ₆ H ₄ NO ₂ COOH	3.0	2.7	2.5	2.2
<i>m</i> -C ₆ H ₄ ICOOH	...	0.5	...	0.4
<i>m</i> -C ₆ H ₄ NO ₂ COOH	0.9	1.0	1.0	1.1

Two further inferences may be drawn from this treatment of acidity. In the first place, it has not been necessary to take into account any transmission of the dipole forces through the electronic structure between the ionizing hydrogen and the polar substituent. This amounts to neglect of the alteration of the induced moments in this region. That the permanent moments predominate is to be expected, since they are, as a general rule, considerably larger than the induced moments. Second, the strengthening effect of unsaturation is due, not to a specific property of the double or triple bond, but to the removal of CH dipoles which, in the saturated acid, are so oriented as to attract the hydrogen ion and thus hinder ionization.

From the foregoing discussion it may be concluded that the change in ionization of an organic acid caused by substitution may be accounted for numerically, at least in the absence of disturbing effects, by assuming as its cause the change in electrostatic repulsion or attraction between the hydrogen ion and the dipoles of the anion of the acid.

In conclusion it is a pleasure to express my indebtedness to Professor K. F. Herzfeld and to Professor J. B. Conant for valuable suggestions in the preparation of this manuscript.

Summary

It has been shown that the changes in ionization of organic acids upon substitution of polar groups are, to a large extent, determined by the magnitude and orientation of the electric moments associated with the substituent groups.

CAMBRIDGE, MASSACHUSETTS