

Electron Spectroscopic Investigations of the Influence of Initial- and Final-State Effects on Electronegativity

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Abstract: Chlorine KLL Auger energies and 2p ionization energies in a variety of compounds have been used to investigate the role of initial- and final-state effects on electronegativity. Compounds studied are HCl, CH₃Cl, C₂H₅Cl, *n*-C₃H₇Cl, *i*-C₃H₇Cl, *t*-C₄H₉Cl, CH_{4-*n*}Cl_{*n*}, CF_{4-*n*}Cl_{*n*}, Cl₂, and ClF. The results obtained (together with similar data on phosphorus and germanium) agree with chemical experience and with theoretical calculations. They show that substituent polarizability (the final-state effect) increases in the order H ≈ F < CH₃ ≈ Cl < Br. The ability of the substituent to create a positive potential at a nearby site (initial-state effect) increases in the order CH₃ < H < Br < Cl < F if the substituent is directly attached to the site and CH₃ < H < Br ≈ Cl ≈ F if the substituent is remote from the site. These results together with related studies of carboxylic acids show that the influence of an alkyl group arises from its ability to disperse charge in the final state and that alkyl groups are either electron donating or electron withdrawing, as their environment demands.

Introduction

The concept of electronegativity, defined by Pauling¹ as the power of an atom in a molecule to attract electrons to itself, has been very useful to chemists. However, an exact, quantitative description of electronegativity remains elusive.

As an example of this elusiveness, it is notable that in the aqueous phase² the acidity of CH₂XCOOH decreases as X is varied from F to I, in keeping with the Pauling electronegativities³ of the halogens, whereas in the gas phase⁴ the order is reversed. In the latter case, the predicted order based on electronegativity clearly conflicts with the measured gas-phase acidities. A similar reversal between gas phase and aqueous phase is found in the acids RCOOH. The aqueous-phase acidities decrease as R is varied from CH₃ to C₃H₇, in keeping with the concept that alkyl groups are electron releasing and become more so with increasing size. In the gas phase, however, the order is once again reversed.⁵

These apparently contradictory observations can be reconciled if we assume that electronegativity arises from two, somewhat related, effects. On the one hand, the atoms compete with one another for electrons; on the other, the atoms are able to accept charge, either positive or negative. In the first, the atoms play an active role. This view is close to the usual concept of electronegativity—the power of an atom to attract electrons to itself. In the second, the atoms are passive; a large, polarizable atom lowers the total energy of the system by either contributing electrons to or receiving electrons from the rest of the molecule.

As an example, consider the substituents fluorine, chlorine, and an alkyl group. The electronegativity of fluorine is dominated by the first factor; it draws electrons strongly to itself but is only slightly polarizable. Chlorine also attracts electrons strongly, but, because of its large size it is more polarizable. In bonding terminology, chlorine is a σ acceptor and a π donor. Alkyl groups do not attract electrons, but are polarizable; the polarizability increases with size. They can, therefore, either give or receive electrons from the surroundings. In this respect, Ingold⁶ has noted that "alkyl groups will exert essentially those polar effects which are impressed on them by the other polar groups present in the molecule".

The ability of a molecule to accept additional charge at a given site, through ionization, protonation, proton removal, or other chemical reactions, is influenced by these two factors in different ways. Conceptually we divide such processes into two steps, (1) the interaction of the new charge with the ground-state, or initial-state, charge distribution of the molecule and (2) the rearrangement of that distribution to accommodate the new charge. Since the ground-state charge distribution is dominated by the competition between the atoms for electrons, it is influenced most strongly by the first of the factors that determine electronegativity, and only to a lesser extent by the second. The rearrangement, or relaxation, of the charge distribution upon arrival of new charge is, on the other hand, determined entirely by the second factor. We can, therefore, approximately equate a substituent's electron-withdrawing power to an initial-state effect and its polarizability to a final-state effect.

This separation of energies into two parts, one due to the initial-state charge distribution and the other to the final-state rearrangement, is similar to that used in theoretical analyses of hydrogen bond energies.⁷ In particular, Kollman and Allen^{7a} have proposed a decomposition of the hydrogen bond energy into an electrostatic-plus-exchange contribution (which depends only on initial-state properties) and a polarization-plus-charge-transfer contribution (which depends on the difference between initial- and final-state properties).

Using these concepts, we can readily account for the relative gas-phase acidities mentioned above. For the acids RCOOH, the initial-state effect is approximately independent of the size of the R group, and the final-state effect, which stabilizes the anion, increases with the size of R.^{5,8} As a result, the predicted anion stabilities and gas-phase acidities are in the order acetic < propionic < butyric, in agreement with experiment. For the halogenated acids, the explanation is essentially the same.⁴ The initial-state effect, though large, is nearly the same for fluorine, chlorine, and bromine. However, the polarizability increases with atomic size, and the acidity increases with the polarizability of the substituent.

In solution, the final-state effect arises from the polarization of the solvent in addition to polarization of the substituent. The solvent effect will be greatest for the smallest substituent, since, in this case, the solvent molecules are closest to the carboxyl anion.

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The effect on acidity of the solvent is, therefore, $F > Cl > Br > I$, which is the reverse of the effect of the substituent itself. In aqueous solution, the polarizability of the solvent dominates and the order of acidity is reversed from that in the gas phase. An alternate but equivalent view is that replacement of a small fluorine atom with a larger halogen also involves displacement of nearby solvent molecules by the halogen. If the halogen is less polarizable than the solvent (as is the case for aqueous solutions), the acidity is lowered. If the halogen were more polarizable, then the acidity would be raised.

Core-ionization energies, measured by X-ray photoelectron spectroscopy (XPS), provide a probe by which these effects can be studied. Early works⁹⁻¹² in this field have shown that there are systematic correlations between the core-ionization energies of a particular atom in a molecule and quantities related to the electronegativities of the substituents. In particular, Thomas¹² showed that the carbon 1s ionization energy in halogenated methanes varies linearly with the electronegativity of the substituents. Later research,¹³⁻²⁰ in particular that by Martin and Shirley¹³ and by Davis and Rabalais,¹⁴ pointed out similar correlations between gas-phase proton affinities (basicities) and core-ionization energies and established the importance of relaxation, or final-state effects, in determining both core-ionization energies and basicities. This approach has been extended to gas-phase acidities by Davis and Shirley²¹ (theoretically) and by Smith and Thomas¹⁹ (experimentally). From comparison of gas-phase acidities and basicities with core-ionization energies, Smith and Thomas determined the relative contributions of initial-state and final-state effects to the gas-phase acidity of a number of carboxylic acids. Their conclusions are in accord with the concepts outlined above.

The core-ionization energies are, like the other chemical properties, affected by both the initial-state charge distribution and the final-state relaxation. Only when other information, such as gas-phase acidities, is available, is it possible to sort out the relative importance of these effects. One source of such information is the Auger kinetic energies for the same atom for which the core-ionization energies have been measured. It has long been recognized that whereas the absolute magnitude of the core-ionization energies and Auger kinetic energies are about equally affected by initial-state effects, the Auger energies are considerably more responsive to final-state effects than are the core-ionization energies.^{22,23} As a first approximation we may express the shift, ΔI , in core-ionization energy between two compounds as

$$\Delta I = \Delta V - \Delta R \quad (1)$$

where ΔV represents the initial-state effect and ΔR the final-state effect. The corresponding expression for the shift in Auger kinetic energies, ΔK , is

$$\Delta K = -\Delta V + 3\Delta R \quad (2)$$

The Auger parameter α , as defined by Gaarenstroom and Win-

Table I. Chlorine 2p Core-Ionization and KLL (¹D) Auger Kinetic Energies (eV)

	compd	2p _{1/2}	2p _{3/2}	KLL
1	CH ₃ Cl	207.90	206.26	2374.51
2	CH ₂ Cl ₂	208.25	206.62	2375.15
3	CHCl ₃	208.50	206.86	2375.52
4	CCl ₄	208.73	207.04	2375.72
5	CCl ₂ F	208.81	207.20	2374.93
6	CCl ₂ F ₂	209.10	207.47	2374.18
7	CCF ₃	209.44	207.83	2373.30
8	Cl ₂	209.45	207.82	2373.72
9	ClF	210.83	209.18	2370.73
10	HCl	209.01	207.38	2371.98
11	C ₂ H ₅ Cl	207.56	205.92	2375.46
12	<i>n</i> -C ₃ H ₇ Cl	207.45	205.81	2375.77
13	<i>i</i> -C ₃ H ₇ Cl	207.25	205.62	2376.17
14	<i>t</i> -C ₄ H ₉ Cl	207.00	205.38	2376.64

ograd,²⁴ is the sum of the core-ionization energy and Auger kinetic energy. Thus

$$\Delta\alpha = 2\Delta R \quad (3)$$

If I and K are measured simultaneously, then charging and reference level effects cancel out in the determination of ΔR . Because of this cancellation, this technique can be, and has been, used to determine relative relaxation energies in solids,^{25,26} even though the relative shifts ΔI and ΔK may be uncertain. The evaluation of ΔV from eq 1 and 2 requires a correct knowledge of both ΔI and ΔK , referenced to the vacuum level, with the result that full exploitation of this technique is limited to gas-phase studies. Few gas-phase measurements of the Auger parameter have been reported,^{20,25,27,28} and, in general, these have focused on ΔR and have not been concerned with ΔV .

We report here the measurement of I and K for chlorine in a variety of compounds RCl and XCl (R = H, CH₃, C₂H₅, *n*-C₃H₇, *i*-C₃H₇, *t*-C₄H₉, CH₂Cl, CHCl₂, CCl₃, CF₃, CF₂Cl, CFCl₂; X = F, Cl). The purpose of this work has been to obtain, through eq 1-3, quantitative information on initial- and final-state effects (ΔV and ΔR), to show that these results are consistent with chemical intuition and simple theory, and further, to determine the relative importance of these two effects on electronegativity. Chlorine is a particularly suitable element for this investigation, since it can be incorporated into a wide variety of molecules.

Experimental Section

All samples were obtained from commercial sources and used without further purification. Measurements on Cl₂ and ClF were made after enough gas had passed through the sample cell so that no evidence of impurities remained. Without such pretreatment, reaction of the sample gas with substances adsorbed on the spectrometer surfaces would give rise to impurity peaks in the spectrum.

X-ray photoelectron and Auger spectra were measured in the Oregon State University cylindrical mirror analyzer.²⁹ Neon was included with the sample gas to provide calibration lines. Aluminum K α X-rays were used to excite the chlorine 2p electrons of the sample and the neon 1s and 2s calibration lines.^{30,31} For the Auger measurements, X-rays from a silver anode were used to excite chlorine KLL Auger electrons, and the calibration was based on the neon KLL (¹D) Auger line³⁰ and the neon 1s line excited by silver L α_1 radiation (2984.31 eV³²). In all of the

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measurements small corrections were made for the recoil energy of the residual ion and for relativistic effects in the analyzer.^{30a} Peak positions were determined by least-squares fits of Gaussian or Voigt functions to the data.

Results

The ionization energies and Auger kinetic energies are summarized in Table I. Each result is the average of at least two measurements. On the basis of the differences between duplicate measurements, we estimate a precision of 0.04 eV for the ionization energies and 0.05 eV for the Auger energies. Particular attention was given to the determination of the Cl₂ and ClF core-ionization energies in order to resolve apparent discrepancies between earlier measurements from this laboratory³³ and later ones by Perry and Jolly.³⁴ Our reported results for these two substances are the average of eight measurements for Cl₂ and six for ClF, of which about half were taken several years ago.³⁵ The value given in Table I for the Cl₂ 2p_{3/2} ionization energy (207.82 eV) is in excellent agreement with that reported by Perry and Jolly³⁶ and corrected by Jolly³⁷ (207.81 eV). For the 2s ionization energy, the new value of 278.71 eV is in good agreement with 278.66 eV given by Carroll and Thomas³³ and 278.74 eV by Holmes.³⁸ For ClF the new value of the chlorine 2s ionization energy (280.08 eV) is in substantial disagreement with the earlier³³ value of 279.23 eV. We cannot account for this discrepancy except to note that ClF reacts readily with adsorbed substances in the spectrometer, giving other chlorine-containing compounds. It is possible that Carroll and Thomas measured the photoelectron spectrum for these reaction products rather than that of ClF.

The 2p_{3/2} ionization energies in Table I for CH₃Cl, CCl₄, Cl₂, ClF, HCl, and (CH₃)₃CCl are in excellent agreement with those given by Perry and Jolly³⁶ and corrected by Jolly.³⁷ The accuracy of our measurements is further supported by a series of six measurements of the argon 2p_{3/2} ionization energy we have made during the course of these experiments. The value of 248.59 eV is in excellent agreement with the value of 248.60 ± 0.05 eV reported by Thomas and Shaw^{30a} and that of 248.62 ± 0.08 eV given by Johansson et al.^{30b} Our value for the Auger kinetic energy in HCl agrees with that given by Cavell and Sodhi³⁹ well within their uncertainties of 0.5 eV.

Theoretical Framework

Equations 1 and 2, upon which our analysis is based, have been derived using both quantum^{23,40} and classical²⁵ approaches. The physical principles involved can be demonstrated by a simple classical model, which is outlined below. A different approach, which includes higher order corrections, is presented elsewhere.⁴¹

The core-ionization energy is the difference between the energy of the initial species (with no core vacancies) and that of the final, core-ionized species. For a neutral free atom we take the first of these energies to be zero and, then, with use of the frozen-orbital approximation, the second is -ε_i, where ε_i is the orbital energy of the ionized electron in the neutral free atom. For a free atom with valence charge⁴² *q* (in units of the electron charge), we still take the first to be zero; the second becomes -ε_i + *k*_i*q*, where *k*_i is a constant.

The orbitals are, however, not frozen, and, for cases of interest here, the atoms are not free. To account for these conditions, we

assume that the initial atom is imbedded in a polarizable medium that produces a potential *V*'/e at this atom. Its energy becomes *qV*'. If no additional polarization took place upon core ionization, *V*' would remain constant, and the energy of the final state would be -ε_i + *k*_i*q* + (*q* + Δ*Z*)*V*', where Δ*Z* is the change in total charge on core ionization (Δ*Z* = 1). This change in charge does, however, cause an additional polarization of the medium with a lowering of the total energy by α'(Δ*Z*)²/2, where α' is proportional to the polarizability of the medium.⁴³ The final state energy⁴⁴ is, then

$$E_f = -\epsilon_i + k_i q + (q + \Delta Z)V' - \alpha'(\Delta Z)^2/2 \quad (4)$$

Subtracting the initial-state energy, *qV*', and setting Δ*Z* = 1, the ionization energy, *I*, is

$$I = -\epsilon_i + k_i q + V' - \alpha'/2 \quad (5)$$

The first three terms on the right represent properties of the initial atom and its interaction with the initial-state charge distribution. We combine *k*_i*q* + *V*' into a single potential energy, *V*. The last term of eq 5 represents the relaxation energy, *R*. Thus

$$I = -\epsilon_i + V - R \quad (6)$$

The Auger transition goes from an initial state with vacancy *i* to a final state with two vacancies *j* and *k*. The initial-state energy is given by eq 4, which is the final-state energy for the photoemission process. The final-state energy for the Auger process, *E*'_f, is

$$E'_f = -\epsilon_j + k_j q - \epsilon_k + k_k q + F_{jk} + (q + 2\Delta Z)V' - \alpha'(2\Delta Z)^2/2 \quad (7)$$

The first pair of terms represents the energy to remove electron *j* from the free atom with charge *q*; the second pair represents the energy for the same process involving electron *k*. *F*_{jk} is the interaction energy between these two electrons. The three terms -ε_k + *k*_k*q* + *F*_{jk} thus give the energy to remove electron *k* from an atom that has already lost electron *j* (in the frozen-orbital approximation). Interaction with the surroundings and relaxation of the passive electrons are accounted for by the remaining terms. It is assumed that the polarizability α' is independent of the total charge on the atom.

We further assume that *k*_i = *k*_j = *k*_k. This assumption is valid if all of the electrons are in the core, as is the case for the systems we have studied. Once again setting Δ*Z* = 1 and subtracting eq 7 from eq 4 to give the Auger kinetic energy, *K*, we have

$$K = -\epsilon_i + \epsilon_j + \epsilon_k - F_{jk} - k_i q - V' + 3\alpha'/2 \quad (8)$$

The first three terms of eq 8 are properties of the free neutral atom, and the fourth is independent of chemical state for core electrons. Combining the first four terms into a single constant, *K*₀, and comparing the remaining terms with those of eq 5 we have

$$K = K_0 - V + 3R \quad (9)$$

In comparisons of core-ionization and Auger energies between different compounds, the constant terms -ε_i and *K*₀ cancel out, giving eq 1 and 2, Δ*I* = Δ*V* - Δ*R* and Δ*K* = -Δ*V* + 3Δ*R*, respectively.

The key assumptions in deriving these expressions are (1) that orbital energies shift linearly with valence charge, (2) that the proportionality constants for these shifts are independent of the core level, (3) that the Coulomb interaction energy, *F*_{jk}, between pairs of core electrons is independent of chemical state, and (4) that the polarizability of the medium is independent of the atomic charge. This last assumption is equivalent to that made by

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(43) The quantity α' is closely related to but not identical with the Auger parameter α. The relationship is established in the subsequent discussion. The factor of 2 has been included to reflect the fact that the total change in energy is half the interaction energy between the charge and the induced field and to eliminate a factor of 2 that would otherwise appear in the relationship between α and α'.

(44) Further refinements to the theory, discussed in ref 40 and 41, take into account that the valence charge *q* changes during core ionization.

Table II. Relaxation Energies and Initial-State Potentials Derived from the Auger Parameter Relative to CH₃Cl (eV)

compd	ΔR	ΔV
HCl	-0.71	0.41
CH ₃ Cl	0	0
CH ₂ Cl ₂	0.50	0.86
CHCl ₃	0.81	1.41
CCl ₄	0.99	1.77
CClF ₃	0.19	1.76
CCl ₂ F ₂	0.44	1.65
CCl ₃ F	0.69	1.65
CCl ₄	0.99	1.77
Cl ₂	0.39	1.95
ClF	-0.43	2.49
CH ₃ Cl	0	0
C ₂ H ₅ Cl	0.31	-0.03
<i>n</i> -C ₃ H ₇ Cl	0.36	-0.08
<i>i</i> -C ₃ H ₇ Cl	0.52	-0.12
<i>t</i> -C ₄ H ₉ Cl	0.63	-0.25

Shirley,²³ in the corresponding quantum mechanical derivation, that V^*-V , the polarization potential due to a transition from 0 to 1 core vacancies, is equal to $V^{**}-V^*$, the polarization potential due to a transition from 1 to 2 vacancies.

In eq 6 and 9, R includes both atomic and extraatomic relaxation. It is assumed that the atomic relaxation is constant as an atom is shifted from one environment to another; consequently, ΔR of eq 1 and 2 depends only on the extraatomic relaxation, which in turn reflects the polarizability of the surrounding molecules.

As was noted in the introduction, combination of eq 1 and 2 leads to the relationship between the Auger parameter, α , and the relaxation energy, R , $\Delta\alpha \equiv \Delta I + \Delta K = 2\Delta R = \Delta\alpha'$ (eq 3). We see here that the relative Auger parameter is identical with the relative polarizability, $\Delta\alpha'$. The relationship between $\Delta\alpha$ and ΔR , eq 3, has not been verified experimentally. Adams⁴⁵ has theoretically calculated both $\Delta\alpha$ and ΔR for a number of chlorine-containing compounds and found that these values scatter fairly close to the line predicted by eq 3. The average difference between ΔR and $\Delta\alpha/2$ is 0.24 eV.

Siegbahn and Goscinski⁴⁰ have proposed further refinements to this model, taking into account that the relaxation during core ionization transfers charge to the ionized atom (in addition to polarizing the surroundings). In this case, the q 's of eq 4 and 7 are not equal to one another nor to the charge of the original atom. Thomas⁴¹ has considered the same problem from a different point of view. According to his results, the relationship between the Auger parameter and the relaxation energy is

$$\Delta\alpha = 2 \left[\Delta R - \frac{2}{3} \Delta \frac{dk}{dN} \frac{dq}{dN} \right] \quad (10)$$

where N is the number of core electrons, k is the proportionality constant between valence charge and potential energy of an electron (as in eq 4), and q is the valence charge. A very similar expression is given by Siegbahn and Goscinski, who also note that this additional term is large in some cases, amounting to 2.5 eV between CS₂ and SF₆. It will be seen below, however, that this correction is relatively small for the systems we are considering.

Discussion

The values of ΔR and ΔV (relative to those for CH₃Cl) determined from our measurements of ΔI and ΔK together with eq 1 and 2 are given in Table II. The entries are grouped to facilitate comparisons between similar compounds.

Hydrogen-Methyl Shift. The comparison of HCl with CH₃Cl and the series of compounds (CH₃)_{3-*n*}CH_{*n*}Cl show the effect of hydrogen vs. methyl. As expected, ΔR for hydrogen is negative compared to that of methyl, reflecting the greater polarizability

of methyl. The sign of ΔV is positive for HCl. Both of these results agree with those obtained by Smith and Thomas¹⁹ from comparisons of core-ionization energies with gas-phase acidities of carboxylic acids, and with those obtained by Ashe et al.²⁰ from comparison of AsH₃ with As(CH₃)₃. It is important to note that a positive ΔV does not necessarily imply that, in the ground state, hydrogen gives up negative charge to chlorine less readily than does methyl. V/e is the potential at the chlorine center and reflects not only the charge on the chlorine but also the field caused by surrounding charges. In methyl chloride, the positive charge is more delocalized and less effective at producing a positive potential at the chlorine than is the charge on hydrogen in HCl. CNDO/2 calculations indicate that the charge on chlorine in the two compounds is nearly the same and the ΔV arises largely from such delocalization. Recent calculations by Wiberg,⁴⁶ which indicate that the carbon in methyl chloride is negative, also support this view. (A similar situation exists for CF₃, which appears to be slightly electron donating but which produces a strong positive potential at an adjacent atom.⁴⁷)

Hydrogen-Fluorine Shift. The effect of replacing hydrogen with fluorine can be seen by comparing HCl with ClF or by comparing CH₃Cl with CF₃Cl. In each case we see that the change in ΔR is relatively small, +0.28 eV for the first comparison and +0.20 eV for the second. This small ΔR is consistent with the results obtained by Smith and Thomas. There is apparently little difference between the polarizability of H and F in these substances. This result explains why models that ignored relaxation could be applied to fluorinated hydrocarbons successfully.^{12,48,49} The differential relaxation effects in such substances are small. The ΔV term is, as expected, large and positive. The presence of the fluorine atoms produces a positive potential at chlorine, either by direct withdrawal of electrons from the chlorine (as in ClF) or by withdrawal of electrons from the adjacent carbon (as is probably the case in CF₃Cl⁴⁷).

Hydrogen-Chlorine Shift. The comparison between HCl and Cl₂ and comparison within the series of compounds CH_{4-*n*}Cl_{*n*} show the effect of replacing hydrogen by chlorine. Because of the high polarizability of chlorine there is a large increase in relaxation energy between HCl and Cl₂ and also through this series. Similarly, because chlorine attracts electrons more strongly than does hydrogen, there is a corresponding increase in ΔV . These conclusions agree with those obtained by Smith and Thomas¹⁹ in a comparison of the core-ionization energy and gas-phase acidity of CH₃COOH with those of CH₂ClCOOH.

The overall relaxation per chlorine is less in the halogenated methanes than in Cl₂, presumably because of the greater chlorine-chlorine distances in the methanes. The positive charge on the core-ionized atom in these compounds is less effective at polarizing the neighboring chlorines and interacts less effectively with the induced field than does the charge on the corresponding chlorine in Cl₂. According to a simple model,^{8b} the total interaction energy should fall off as the fourth power of the distance. We note also that there is an apparent saturation of the relaxation energy in the chloromethanes. Although ΔR and ΔV increase with the number of chlorine atoms, the first spectator chlorine (in CH₂Cl₂) is nearly twice as effective as additional chlorines. Such saturation is in disagreement with the model given by Bahl et al.,^{26b} which predicts a linear relationship between the total relaxation energy and the number of chlorines.

Chlorine-Fluorine Shift. Information on the chlorine-fluorine shift comes from the series CCl_{4-*n*}F_{*n*}, in which chlorines are replaced by fluorines, and from the comparison of Cl₂ with ClF. The relaxation energies are unambiguous; replacement of fluorine by more polarizable chlorine increases the relaxation energy. The effect is largest when the chlorine-chlorine distance is smallest,

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as is the case for replacing hydrogen with chlorine. Saturation of ΔR is not apparent in this series.

The values of ΔV for these compounds are of particular interest. Between Cl_2 and ClF there is a significant increase in ΔV , indicating that fluorine withdraws electrons from chlorine, in keeping with chemical intuition. There is, however, almost no effect on the value of ΔV from exchanging chlorine for fluorine on the halogenated methanes. A similar result has been reported by Smith and Thomas,¹⁹ who found from studies of halogenated carboxylic acids (CH_2XCOOH) that $\Delta V_{\text{F}} = \Delta V_{\text{Cl}} = \Delta V_{\text{Br}} = 0.45$ eV.

We see from foregoing observations that the relative effects of halogen substituents depend on whether they are attached directly to the atom of interest, as in ClF , or remotely, as in CX_3Cl or CH_2XCOOH . In the first case, the relaxation contribution increases and the initial-state effect decreases as we go from F to Cl. If, however, the halogen is remote to the atom of interest, then the initial-state effect is the same for fluorine, chlorine, and bromine, and only the relaxation effect varies. This conclusion is completely in accord with the view expressed by Hiraoka et al.,⁴ that the relative gas-phase acidities of the halogenated carboxylic acids are dictated by the relative polarizabilities of the halogens.

Chlorine-Methyl Shift. Comparison of CH_3Cl with Cl_2 , of $\text{C}_2\text{H}_5\text{Cl}$ with CCl_2H_2 , of $i\text{-C}_3\text{H}_7\text{Cl}$ with CCl_3H , and of $t\text{-C}_4\text{H}_9\text{Cl}$ with CCl_4 shows that the relaxation energy for chlorine is greater than that for methyl. The difference is, however, small except in the first case, where the substituent is close to the atom of interest. The results of Smith and Thomas¹⁹ for CH_2ClCOOH and $\text{C}_2\text{H}_5\text{COOH}$ indicate that chlorine and methyl have about the same relaxations. The same set of comparisons shows that ΔV is much larger for chlorine than for methyl.

Fluorine-Methyl Shift. The fluorine-methyl shift can be determined by comparison of ClF with CH_3Cl and CClF_3 with $t\text{-C}_4\text{H}_9\text{Cl}$. ΔR for methyl is greater than that of fluorine and ΔV is less, as expected.

Alkyl Groups. The series of compounds RCl with $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, and $t\text{-C}_4\text{H}_9$ shows that ΔR increases with the size of the alkyl group. There is, however, only a slight variation in ΔV through the series. Both of these results agree with those obtained by Smith and Thomas from a comparison of CH_3COOH with $\text{C}_2\text{H}_5\text{COOH}$.

In a theoretical investigation of the proton affinities of alkyl halides,⁵⁰ Jorgensen has found that "the proton affinities of alkyl chlorides are controlled by the ability of the alkyl group to accommodate (the) positive charge" of the additional proton. Since protonation and core ionization both correspond to addition of a positive charge at the halogen and the subsequent redistribution of that charge over the molecule, there is a close correspondence between the factors that govern proton affinities and those that govern core-ionization energies.¹³⁻²⁰ What Jorgensen describes as the ability of the alkyl group to accommodate positive charge, we describe as the contribution of the alkyl group to the relaxation energy. Since the variation of ΔV through the series of alkyl halides is negligible our conclusion is the same as that of Jorgensen.

The effect of an alkyl group on the gas-phase acidity of carboxylic acids is, as noted in the introduction and verified by the measurements of Smith and Thomas, to stabilize the anion by dispersing the negative charge over itself. In this case, the alkyl group acts as an electron acceptor. During core ionization, as studied here, or in protonation,¹³ the alkyl group stabilizes the final state by dispersing a positive charge over itself. Here the alkyl group acts as an electron donor. Thus, depending on the environment, alkyl groups act readily as either electron donors or electron acceptors. They generally behave as electron donors because, as Ingold⁵¹ has pointed out, "the majority of commonly encountered substituents are attractors of electrons".

Comparisons with Other Work. Perry and Jolly²⁷ have measured the Auger parameter for a series of substituted germanes and have analyzed the results in terms of relaxation energies. Their

Table III. Final-State Relaxation Energies (ΔR) and Initial-State Potentials (ΔV) for Germanium and Phosphorus Compounds (eV)

compd	ΔR	ΔV
Germanium ^a		
GeH_4	0	0
$\text{GeH}_3(\text{CH}_3)$	0.30	-0.16
$\text{Ge}(\text{CH}_3)_4$	0.94	-0.33
GeH_3Br	0.53	1.28
GeH_3Cl	0.39	1.26
GeBr_4	1.44	3.49
GeCl_4	1.10	3.80
GeF_4	-0.29	4.36
Phosphorus ^b		
PH_3	0	0
PCl_3	1.6	4.4
PF_3	0.1	4.8
SPCl_3	2.2	6.0
SPF_3	1.3	6.8
OPCl_3	1.7	5.7
OPF_3	0.4	6.3
PF_5	0.8	9.1

^a Data from ref 27. ^b Data from ref 39 using phosphorus 2p core-ionization energies.

data together with values of ΔV , which were not included in their work, are summarized in Table III.

The conclusions to be drawn from the germanium results are very similar to those based on our measurements. The first three lines of Table III show the greater polarizability of methyl compared to hydrogen and that hydrogen creates a more positive environment at the germanium atom than does methyl. Comparison between GeH_4 and GeF_4 shows that the relaxation difference between hydrogen and fluorine is small (although of opposite sign to what we have observed). The relaxation differences between the halogens are large whereas the differential effects on the initial-state potential are relatively small. There is some evidence for the saturation of relaxation energy mentioned above. Some of these conclusions were noted by Perry and Jolly, who also pointed out that the order of polarizabilities derived from their results ($\text{F} < \text{H} < \text{CH}_3 < \text{Cl} < \text{Br}$) is consistent with optically determined polarizabilities. This is the same order as determined in our measurements except that we find $\text{H} \approx \text{F}$.

Also summarized in Table III are values of ΔV and ΔR calculated from the phosphorus KLL Auger kinetic energies and 2p core-ionization energies reported by Cavell and Sodhi.³⁹ The conclusions are basically the same. The order of polarizabilities is $\text{H} \approx \text{F} < \text{Cl}$. The values of ΔV for chlorine are, however, about the same as those for fluorine. We note that ΔR for sulfur is slightly greater than ΔR for oxygen, as might be expected.

Measurements of the Auger parameter for tellurium compounds have been reported by Bahl et al.^{26b} Since the measurements were made in the solid phase, no ΔV information is available. The order of relaxation energies is hydrocarbon $< \text{OH} < \text{Cl} \approx \text{O} < \text{Br} < \text{I}$, which agrees with the order we have found.

Comparison with Theoretical Models

Adams⁴⁵ has calculated total relaxation energies for chlorine in several compounds by using a contracted Gaussian basis set. Relative to CH_3Cl , these calculations give extraatomic relaxation energies of -0.77 eV for HCl and -0.50 eV for ClF , which compare favorably with the corresponding experimental values of -0.71 and -0.43 eV from Table II. The overall shifts in 2p ionization energies calculated by Adams are 1.48 eV for HCl and 2.84 eV for ClF , compared with experimental values of 1.12 and 2.92 eV, respectively.

Potential models have been developed by Davis and Shirley⁵² with which it is possible to calculate ΔR and ΔV and, hence, ΔI and ΔK . Using these models and the CNDO/2 approximation (without d orbitals), we have calculated these quantities.

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(51) Reference 6, p 81.

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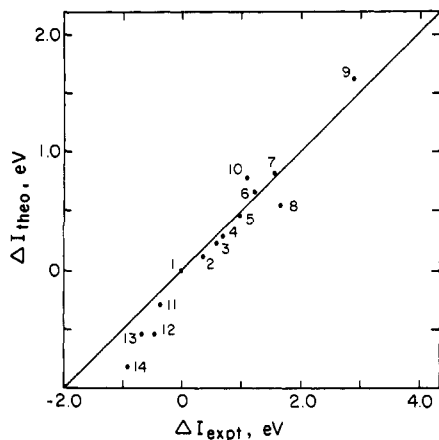


Figure 1. Chlorine core-ionization energy shifts calculated by using the relaxation-potential model and CNDO/2 wave functions plotted against the experimental shifts.

Figure 1 shows the theoretical shifts ($\Delta V - \Delta R$, or relaxation-potential model, RPM), relative to CH_3Cl , vs. the experimental shifts. The line has a slope of 1.00. Although there is some scatter about this line, it is clear that the theoretical model predicts the trend of the data. A least-squares fit to these points has a slope of 1.23.

A similar comparison has been made by Cavell and Sodhi³⁹ of phosphorus 1s and 2p experimental core-ionization energies with values from RPM calculations. A plot similar to that of Figure 1, with use of their data, shows comparable scatter and least-squares slopes of 1.13 for the 1s electron and 1.34 for the 2p. Cavell and Sodhi attribute the difference between these two slopes to "the more pronounced interaction of the 2p electrons with the valence shell electrons as compared to the 1s electrons". A similar effect might be important for the chlorine 2p electrons. These, however, have significantly higher ionization energies than do the phosphorus 2p electrons (207 eV for HCl compared with 137 eV for PH_3) and, therefore, are more corelike. This view is supported by the theoretical calculations of Adams,⁴⁵ which show that the chlorine 1s shifts are about 6% greater than the chlorine 2p shifts. The corresponding difference in phosphorus is 16% from the data of Cavell and Sodhi. An analysis we have presented elsewhere⁴¹ suggests that, to correct for this effect, the chlorine 2p shift should be reduced by 6% before calculating $\Delta\alpha$. The effect of this correction of ΔR is about 0.09 eV for ClF and is less for all of the other compounds.

A comparison between experimental relaxation energies (relative to CH_3Cl) and those from RPM and GPM (ground-state potential model⁵²) calculations using CNDO/2 wave functions is shown in Figure 2. Except for HCl the agreement is reasonably good, although the data deviate slightly from the line of unit slope. Consideration of higher order corrections⁴¹ to eq 3 indicates that this method will give relaxation energies that are too high in proportion to the relaxation energy (eq 10 of this work). The deviation of the data (except for HCl) from the calculated values is in this direction.

A more quantitative analysis of the higher order terms⁴¹ gives eq 10. The quantity dk/dN is negative and dq/dN is positive. The overall error is positive. The second factor, dq/dN , is the change in valence charge on core ionization and is easily obtained from the CNDO/2 calculations for the initial molecule and the core-ionized species (using the equivalent-cores approximation).

We can estimate values of k for Cl and its core-ionized species Cl^{*+} with the equivalent-cores approximation,⁵³ giving $dk/dN = -4$ eV/atomic charge unit. Siegbahn and Goscinski⁴⁰ have obtained values of k by using the orbital exponents ζ for the appropriate Slater orbital. For $n = 2$ orbitals $k = \zeta/2$ and ζ increases by $1/2$ as the core charge changes by 1. Hence, dk/dN

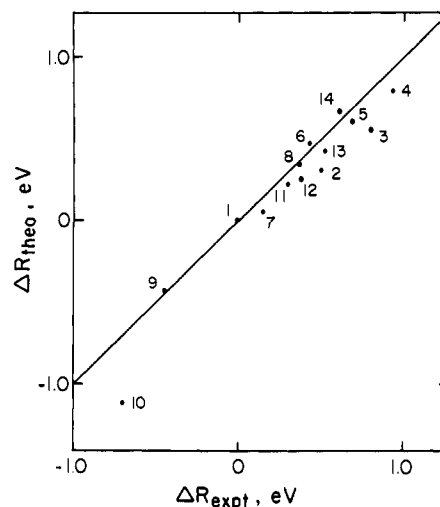


Figure 2. Theoretical relaxation energies plotted against those determined from the Auger parameter.

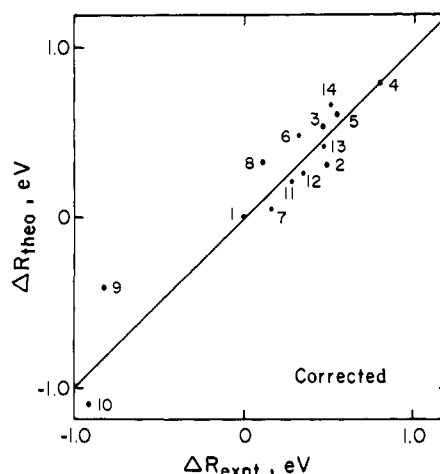


Figure 3. Theoretical relaxation energies plotted against those determined from the Auger parameter with higher order corrections.

$= -1/4 \text{ au} = -7 \text{ eV}$. Taking the first estimate, -4 eV , which is based on experimental quantities, we obtain the correction term for ΔR as $8/3 \Delta(dq/dN)$.

We have applied the correction to the relative relaxation energies determined from the Auger parameter by using values of dq/dN from the CNDO/2 calculations. The results are compared with the theoretical calculations in Figure 3; the slope is now much closer to 1. The absolute values of the corrections are significant, about 0.4 eV for CCl_4 . The relative corrections are, however, small, ΔR for CCl_4 changing from 0.99 to 0.80. The qualitative conclusions are unchanged.

It is interesting to note that the theory predicts the general trend of the relaxation energies (Figure 3) more accurately than it does the shifts in ionization energy (Figure 1). The former depend only on changes in the potential during ionization, whereas the latter depend also on the absolute value of the potential. Presumably, there are systematic errors in the absolute potentials that cancel when the changes in the potential are calculated.

Conclusions

The chemical effects that are included within the qualitative concept of electronegativity arise from two sources. First, a substituent affects the ground-stage charge distribution in the molecule by its ability to attract electrons to itself. Second, the ability of a molecule to accept charge (through protonation, proton removal, or ionization, for example) is influenced by the ability of the substituent to delocalize this charge.

Core-ionization energies and Auger kinetic energies can be combined to give direct and quantitative measurements of these

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properties. The results obtained are in good agreement with chemical experience and simple theory. In particular, they show that the relaxation effect increases in the order $H \approx F < CH_3 \approx Cl < Br$. For alkyl groups the contribution increases with the size of the group. The relaxation energy decreases with distance between the substituent and the site at which the charge is being changed. For the initial state, the effect depends on whether the substituent is attached directly to the atom of interest or is more remote in the molecule. In the first case, the order is $CH_3 < H < Cl < Br < F$; in the second, $CH_3 < H < Cl \approx Br \approx F$. The striking results here are that hydrogen produces a more positive environment than does methyl and that halogens in remote positions affect the ground-state potential about equally.

The influence of an alkyl group on the initial-state charge distribution is, by definition,⁶ essentially neutral. The effect of alkyl groups arises from their polarizability, or, equivalently, their ability to disperse charge. Comparison of the results obtained here with those from studies of carboxylic acid shows that an alkyl group can act either as an electron acceptor or as an electron donor, depending on the sign of the charge that must be dispersed.

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Liquid Crystalline Phases of the Sodium Decyl Sulfate/Decanol/Water System. Nematic-Nematic and Cholesteric-Cholesteric Phase Transitions

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Abstract: The existence of a thermally induced phase transition between two nematic phases in the ternary mixture of sodium decyl sulfate, decanol, and water is verified by microscopic studies and deuteron resonance of D_2O . The phase diagram over the range that gives two nematic phases is reported as a function of temperature and water to sodium decyl sulfate ratio keeping the weight percent of decanol constant. The lower temperature nematic (N_L) possesses a negative diamagnetic and a positive optical anisotropy, the higher temperature nematic (N_C) a positive diamagnetic and a negative optical anisotropy. Our results indicate that the N_L phase has micelles of a bilayer structure and the N_C phase micelles of a cylindrical structure. Two cholesteric phases are obtained by adding a chiral compound into the mixture exhibiting the aforementioned nematic phases. The responses of the cholesterics to a magnetic field and the thermally induced phase transition between them are observed. The twist induced in the bilayer micelle phase is twice that of the cylindrical micelle phase at equal concentration of added chiral compound.

I. Introduction

A nematic phase in aqueous solutions of sodium decyl sulfate (NaDS) and decanol was first reported by Lawson and Flautt,¹ who used it as a solvent for NMR spectroscopy. Radley and Reeves² found that the system forms two different nematic phases. They showed by NMR studies that a direct, thermally induced transition between the two phases can be observed. The diamagnetic anisotropy changes its sign at the transition. It is negative for the lower temperature phase and positive for the higher temperature phase.

The two phases are perhaps best described as anisotropic micellar solutions which differ in the structures of the micelles.³ Our studies indicate that the high-temperature nematic phase has rod-like micelles of a structure similar to the surfactant aggregates in the normal hexagonal smectic phase or middle soap. The low-temperature phase, on the other hand, has disk-like micelles of a structure similar to the bilayers in the lamellar smectic phase or neat soap.

We will refer to these two nematic phases as N_C and N_L phase, respectively. They correspond for the given system to type I and type II nematic, respectively, as defined by Reeves and co-workers,^{2,4-6} but the assignment may have to be changed for other

Table I. Concentrations of the Components of the Ternary Mixture

sample no.	concn, wt %		
	D_2O	decanol	NaDS
1	58.54	6.99	34.47
2	58.0	7.0	35.0
3	57.53	7.0	35.47
4	57.05	7.0	35.95
5	56.5	7.0	36.5
6	56.0	7.0	37.0
7	57.52	7.19	35.29
8	58.02	6.80	35.18
9	55.97	7.21	36.82
10	56.51	6.79	36.70
11	54.97	7.07	36.96

systems.³ An N_L phase is transformed to a cholesteric phase by addition of a chiral compound.⁷ It twists about as readily as a thermotropic nematic phase. The response of an N_C phase to chiral compounds has not been studied earlier.

It is the purpose of this paper to provide more evidence on the nematic phases in the NaDS/decanol system. A section of the phase diagram of the D_2O /NaDS/decanol system focused on the range of the nematic phases along with the various surrounding phases is given. It is demonstrated that the addition of a chiral compound induces in both cases the formation of cholesteric phases and that a thermally induced transition between the two cho-

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