(3) The $^{1,3}A_1$ states of the isolated complex are bound by about 0.8 eV with respect to the separate fragments, Co(foracim)$_2$ and Li, and are characterized by a relevant electronic σ-donation from the organic ligand to the cobalt and by a simultaneous expansion of the π-system.

(4) The $^1A_1$ closed-shell state exhibits an appreciable electronic π-back-donation from the cobalt to the ligand, with a reduced σ-donation from the ligand to the cobalt.

Finally, we observe that, at least a part of these results, which refer to the isolated molecule, can also be ascribed to the choice

of lithium as the alkali-metal atom, its ionization potential being appreciably higher than that of the other alkali-metal atoms.

The Role of Resonance and Inductive Effects in the Acidity of Carboxylic Acids

Michele R. F. Siggel, Andrew Streitwieser, Jr.,* and T. Darrah Thomas[1]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received February 19, 1988

Abstract: The normal inductive effects are shown to account for most of the enhanced acidity of carboxylic acids compared to alcohols. The contributions of these effects are determined using several extrapolations from nonconjugated systems. Further support is given from atomic population analyses of formic acid, formate ion, ethanol, and ethoxide ion. A comparison of the natural population analysis, integrated projection populations, and integrated Bader populations is given as well as the effects of varying the basis set (3-21+G, 6-31+G, 6-31+G*). Qualitatively, all population analyses agree that the carbonyl group in carboxylic acids is highly polarized and is the major contribution affecting the relative acidities of carboxylic acids and alcohols. Vinyl alcohol and vinyl alkoxide are included in the population analysis for comparison.

The greater acidity of carboxylic acids compared to alcohols is normally ascribed in current textbooks primarily to the resonance energy or, equivalently, increased charge delocalization in carboxylate ions compared to alkoxide ions; that is, in a carboxylate ion the charge is divided between two oxygens whereas in the alkoxide ion it is localized on only one.[2] This traditional view has been challenged by Siggel and Thomas[3] who found from a comparison of experimental photoelectron core-ionization energies with gas-phase acidities as well as from ab initio calculations that the gas-phase acidity difference between an alcohol and a carboxylic acid is determined by the potential at the proton in the neutral acid. That is, the acidity difference is already fully inherent in the ground-state electronic properties and is not due to differential effects in the product anions. This view was confirmed by our recent studies of projected electron density functions and difference functions of ethanol and formic acid and their anions.[4] The results of this study indicate that the carbonyl group is already so polar that little additional delocalization of charge can occur to the carbonyl oxygen.

In this paper we show that normal inductive effects can account for most of the enhanced acidity of carboxylic acids compared

**Table I.** Correlation of Gas-Phase Acidities of Some Alcohols with σ_1

alcohol	$\sigma_1{}^a$	$\Delta H_{acid}{}^b$
CH$_3$CH$_2$OH	-0.01	376.1
MeOCH$_2$CH$_2$OH	0.11	372.5
F$_2$CHCH$_2$OH	0.32	367.0
CF$_3$CH$_2$OH	0.40	364.4

^{a}Reference 8. ^{b}In kcal mol^{-1} from ref 7.

to alcohols and confirm that the charge delocalization in carboxylate ions plays only a small role.

Inductive Effect of the Carbonyl Group

The new view assigns a much greater role to inductive effects than has been recently generally accepted. However, the inductive effect of a nearby polar carbonyl group had been considered as a significant factor in early theoretical studies. For example, in discussing the role of carboxylate resonance, Wheland recognized that inductive effects could be important: "...resonance of the present type may make a considerable contribution to the relatively great acid strength, *although the closeness of the large carbonyl group moment makes a decision difficult* (emphasis ours). Both the electrostatic and the resonance factors operate here to increase the acidity, and we cannot be sure how much of the observed effect must be attributed to each cause."[5] Pauling also wondered about the relative importance of resonance structure 1 in making the

1
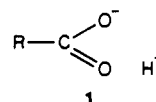
hydrogen more acidic and emphasized that the resonance energy of RCO$_2^-$ is not known; however, he also wrote (regarding structure 1), "The concept of resonance provides an obvious ex-

(1) Department of Chemistry, Oregon State University, Corvallis, OR 97331.

(2) Some currently popular textbooks using essentially this argument are: Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn & Bacon: Boston MA, 1983; p 793. Solomons, T. W. G. *Fundamentals of Organic Chemistry*; Wiley: New York, 1982; p 602. Loudon, G. M. *Organic Chemistry*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1987; p 825. Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; MacMillan: New York, 1985; pp 452-3. Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1977; pp 797-8. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 6. Wade, L. G., Jr. *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1987; p 979. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 231.

(3) Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* 1986, *108*, 4360.

(4) Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A., Jr. THEOCHEM 1988, *165*, 309.

(5) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: 1955; p 345.

Inductive Effects in Acidity of Carboxylic Acids

J. Am. Chem. Soc., Vol. 110, No. 24, 1988 8023

planation of some of the characteristic properties of the carbonyl group, the most striking of which is its acid strength. If the electronic structure of a carboxylic acid were $RC(=O)OH$, its acid strength would differ only by a rather small amount from that of an alcohol."[6]

When a substituent is conjugated to a reactive center, it is difficult to separate resonance from inductive effects. It is difficult, if not impossible, to do so in any rigorous way when the substituent is also as close to the reactive center as the carbonyl group is to the hydroxy group in a carboxylic acid. The best one can do is to get a rough measure of the effect by extrapolation from non-conjugated systems. The results of some such extrapolations follow.

Gas-phase acidities are now known for a number of alcohols[7] and permit correlations with appropriate inductive substituent constants. The gas-phase acidities summarized in Table I together with the σ_1 constants of Charton[8] give an excellent linear correlation ($r = 0.999$), $\Delta H^{\circ}_a = 375.75 - 28.04\sigma_1$ kcal mol^{-1}, for the series YCH_2OH. The alcohols were chosen to be of comparable size in order to minimize the polarizability effects that have been shown to be important in the gas phase.[9] For example, benzyl alcohol would be expected to be more acidic than such an inductive treatment would predict, and it is by 2.7 kcal mol^{-1} (calcd, 372.3; exptl, 369.6). We use this relationship to predict the magnitude of the inductive effect of the carbonyl group on the acidity of acetic acid. We do this by considering CH_3COCH_2OH, for which there is no conjugative effect, and then correcting for the weakening of the inductive effect because of the intervening CH_2 group. The ratios of σ_1 values, $Y-/YCH_2-$, for a number of substituents in Charton's tables range from about 2.4 to 2.8. The acetyl group has $\sigma_1 = 0.30$.[8] We, therefore, use as a rough measure of the change from CH_3CO-CH_2-OH to CH_3CO-OH the factor 2.6 which is about the average for the effect of moving the substituent away from the reactive center by an additional methylene group. This gives an "effective" σ_1 for acetic acid of 0.8 and a corresponding calculated gas-phase acidity, ΔH°_a, of 353 kcal mol^{-1}, less than 5 kcal mol^{-1} higher than the experimental value of 348.5 kcal mol^{-1}. The factor of 2.6 may well be too low, and if so then the calculated ΔH°_a would be still lower. Since inductive effects are primarily through-space electrostatic interactions involving substituent dipoles, the distance effect becomes more important as one approaches the substituent. Nevertheless, even the crude extrapolation given above shows that the simple "inductive effect" of the carbonyl group can account for more than 80% of the increased acidity of acetic acid over ethanol; that is, an electrostatic model of the carbonyl–hydroxy interaction based on nonconjugated reference systems gives sufficient enhanced acidity that relatively little additional acidity enhancement is left for other interactions.

An alternative approach to determining the overall contribution of carboxylate resonance to the acidity of carboxylic acids involves the comparison of gas-phase acidities for a series of molecules such as ethane (421 kcal mol^{-1}),[10] ethanol (376 kcal mol^{-1}),[7] formaldehyde (392 kcal mol^{-1}),[11] and formic acid (345 kcal mol^{-1}).[7] Oxidation of ethane and formaldehyde gives ethanol and formic acid, respectively. The enhanced acidity of ethanol relative to ethane, 45 kcal mol^{-1}, can be attributed entirely to the electronegativity effect of the oxygen in ethanol. Comparing the acidity of formic acid with that of formaldehyde compensates approximately for the inductive effect of the carbonyl group; the difference of 47 kcal mol^{-1} is only 2 kcal mol^{-1} greater than the acidity difference between ethane and ethanol and represents approximately the amount to be attributed to conjugative interaction. The resulting number is entirely consistent with the result of the

previous paragraph, which gave an estimate of less than 5 kcal mol^{-1}. (Note, if an extreme value for the ratio of σ_1 for $Y-/YCH_2-$ of 2.8 were used, then the "effective" σ_1 for acetic acid would be 0.87 corresponding to a calculated gas-phase acidity of 351 kcal mol^{-1}, only 3 kcal mol^{-1} higher than the experimental value.)

This same result can be obtained by comparing the acidity difference of ethane and formaldehyde, 29 kcal mol^{-1}, with the acidity difference of ethanol and formic acid, 31 kcal mol^{-1}. As in the first comparison, the resonance contribution to the enhanced acidity of formic acid is given by the difference, 2 kcal mol^{-1}, or about 6% of the difference between ethanol and formic acid.

This dominating role of inductive effects on the acidity of carboxylic acids is actually foreshadowed by the work of Branch and Calvin who, almost half a century ago, suggested an empirical equation that allowed the estimation of the aqueous pK_a's of a number of inorganic acids for which resonance was thought not to be important.[12] The method applied to formic acid with a polarized carbonyl group gave a predicted pK_a of 7.3 (exptl 3.75[13]) compared to the predicted pK_a of methanol of 16.4 (exptl 15.5[14]). Thus, their approach, using only simple inductive parameters, accounts for almost 80% of the difference in acidity between formic acid and methanol. Application of the Branch and Calvin procedure to the first and second dissociation constants of carbonic acid is even more dramatic; their method applied to $^-O-C^+(OH)_2$ predicts a pK of 5.6 (exptl 3.7) and for $HOC^+O_2{}^{2-}$ predicts 10.5 (exptl 10.3). This agreement confirms the general applicability of this empirical procedure and the high polarity of the carboxylic acid group.

The above discussion has shown that the inductive effect of the carbonyl group suffices to explain most of the enhanced acidity of carboxylic acids compared to alcohols and that the energy consequences of carboxylate resonance are comparatively small. We next turn to the second aspect of such resonance, its effects on charge distribution.

Population Analysis and Charge Distribution

The concept of "atomic charge" in molecules has been a useful qualitative tool for chemists in characterizing the nature of bonding, in explaining the reactivities of molecules, and in discussing reaction mechanisms. Discussions in textbooks[2] of charges in carboxylate groups provide apt examples. Yet, it has proven difficult to quantify the notion of "atomic charge" in a satisfactory way within the framework of quantum chemistry because the atomic charge is not a physical observable and is not, therefore, defined as the expectation value of some quantum mechanical operator. Two fundamentally different approaches have emerged from the attempt to define atomic charges in terms of the molecular wave function. The partitioning of the molecular electron density is done (a) either in the real three-dimensional Cartesian space or (b) in the Hilbert space spanned by atomic orbital-like basis sets.

In the analysis developed by Bader,[15] a set of partitioning surfaces divides the three-dimensional electron distribution into volumes or "basins". These surfaces start at a saddle point in the electron distribution between a pair of atoms and follow paths of steepest descent through the electron distribution. These surfaces are well-defined mathematically and are spoken of as "zero-flux surfaces" because the derivative of the electron density normal to the surface is zero. Bader has shown that these topologies of the electron density distribution lead to natural definitions of atoms in molecules that have important quantum mechanical properties; for example, the virial theorem applies to these ATOMS (Atoms Topologically Observed in Molecules)[16] as well as to the whole molecule.[17] For convenience, we refer

(6) Pauling, L. *Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1960; p 276.

(7) Reviewed in: Bartmess, J. E.; McIver, R. T., Jr. *Gas Phase Ion Chemistry* Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 87.

(8) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

(9) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.

(10) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1984**, *106*, 4051.

(11) Murray, K. K.; Miller, T. M.; Leopold, D. G.; Lineberger, W. C. *J. Chem. Phys.* **1986**, *84*, 2520.

(12) Branch, G. E. K.; Calvin, M. *The Theory of Organic Chemistry*; Prentice-Hall: New York, 1941; pp 201–211.

(13) Harned, H. S.; Embree, N. D. *J. Am. Chem. Soc.* **1934**, *56*, 1042.

(14) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795.

(15) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9–15, and references therein.

(16) Bader, R. F. W., personal communication.

(17) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1974**, *61*, 2536.

Table II. Optimized Bond Lengths and Angles for Formic Acid, Formate Ion, Vinyl Alcohol, Vinyl Alkoxide, Ethanol, and Ethoxide Ion

	Formic Acid			Formate Ion				Vinyl Alcohol	Vinyl Alkoxide		Ethanol		Ethoxide Ion	
	3-21+G	6-31G*[a]	6-31+G*	3-21+G	6-31G*	6-31+G*		3-21+G	3-21+G		3-21+G	6-31G*[a]	3-21+G	6-31G*
Bond Lengths (Angstroms)														
O4-H5	0.970	0.953	0.954	-	-	-	O4-H7	0.966	-	O2-H9	0.965	0.947	-	-
C1-O4	1.356	1.323	1.322	1.266	1.231	1.235	C1-O4	1.391	1.300	C1-O2	1.459	1.405	1.404	1.312
C1-O3	1.207	1.182	1.183	1.266	1.231	1.235	C1-C3	1.317	1.364	C1-C3	1.521	1.516	1.558	1.556
C1-H2	1.073	1.083	1.083	1.103	1.127	1.117	C1-H2	1.068	1.098	C1-H4&5	1.084	1.089	1.106	1.131
							C3-H5[b]	1.071	1.077	C3-H6	1.085	1.086	1.094	1.096
							C3-H6	1.074	1.076	C3-H7&8	1.082	1.084	1.086	1.090
Bond Angles (Degrees)														
C1-O4-H5	114.74	108.72	109.41	-	-	-	C1-O4-H7	114.91	-	C1-O2-H9	113.57	109.64	-	-
O3-C1-O4	124.22	124.88	124.84	129.64	131.01	130.50	C3-C1-O4	126.16	129.58	C3-C1-O2	106.31	108.04	112.47	113.67
							H2-C1-O4	109.70	115.82	H4&5-C1-O2	109.74	110.60	112.87	115.74
							C1-C3-H5	120.07	120.41	C1-C3-H6	110.43	110.65	112.23	113.67
							C1-C3-H6	122.70	121.37	C1-C3-H7&8	109.98	110.28	109.09	109.48
										H4-C1-H5	109.07	107.51	105.20	101.60
										H7-C3-H8	108.45	108.27	108.01	107.25

[a] Values taken from ref 41.   [b] Trans to oxygen.

to the electron populations that are obtained by integrating over the volumes defined by these surfaces as the "Integrated Bader Populations" or IBP's. The net charge of the atom is given by Z - IBP, where Z is the nuclear charge. The Bader approach has been used in a number of recent investigations and interpretations of chemistry.[18-28] The Bader method has the advantage that it partitions the molecule according to a real physical property of the molecule, the charge distribution. The procedure is independent of the quantum mechanical model that might be used to describe the molecule. As the model becomes more accurate, the derived surfaces and charges will converge to well-defined values.

A disadvantage of the Bader method is that locating the zero-flux surface is not simple and the computation of IBP values is relatively slow and computer intensive. In our past work we have used an approximation to Bader's method that makes use of "projected electron densities". In this approximation, the three-dimensional electron distribution is first integrated in a direction perpendicular to the plane of the molecule to give a two-dimensional, projected electron density.[29] For Gaussian basis sets this integration is analytic and rapid. The two-dimensional surface is partitioned by zero-flux lines,[30] which are, by analogy to the zero-flux surfaces, the lines of steepest descent from the saddle point in the two-dimensional electron distribution; the important difference is that the projection demarcation is a vertical curtain compared to the curved surface of the Bader method. We refer to the resulting populations as Integrated Projection Popu-

lations or IPP's. A disadvantage of this method is that the relative IPP values frequently differ from IBP's and the determination of IPP's for hydrogens is particularly difficult.[31]

The difference between the two procedures is relatively small in ionic systems where the demarcation boundaries involve regions of low electron density, but the differences are greater for bonds with higher covalency; in particular, oxygen populations in different compounds differ significantly by the two procedures.[31] Because of these differences, there may be some question concerning our previous study[4] of the acidities of alcohols and carboxylic acids in which IPP electron populations were used. The present study makes use of IBP values for the discussions of total atomic and group populations and charges.

Of the Hilbert space or basis set population methods, the best may well be the Natural Population Analysis (NPA) method recently proposed by Reed, Weinstock, and Weinhold.[32] The NPA method is an alternative to the Mulliken Population Analysis (MPA) method, and overcomes many of the objections of the MPA method while retaining some of MPA method's advantages. In the NPA, the density matrix is transformed into a set of orthonormal but arbitrary *atomic* (one-center) orbitals that are localized on the individual atoms; the natural atomic orbitals do not transform as symmetry orbitals of the molecule. The occupancies of the natural atomic orbitals, in the system of interest, give the natural (atomic) populations (NPA's). Three advantages of NPA over MPA are (1) NPA populations are relatively insensitive to the choice of basis set whereas MPA's are unduly sensitive to basis set, (2) NPA's are inherently positive whereas MPA's can be unreasonably negative, and (3) the NPA tends to give reasonable populations for ionic systems whereas MPA often does not. An advantage of both the MPA and NPA methods is that they are relatively fast and not very computer intensive.

Molecular and Ionic Geometries. The molecular and ionic conformations used in this study are shown in Figure 1; these represent the lowest energy conformation for each species. The geometries of all species were optimized using GAUSSIAN 82[33] with C_s symmetry imposed. The largest basis set used was 6-31+G*, a 6-31G* basis set[34] with an added diffuse sp shell as recommended by Clark et al. for anions.[35] The resulting structures for formic acid and formate ion differ little from the 6-31G* structures.[23,36]

(18) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.

(19) MacDougall, P. J.; Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1496-1508.

(20) Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1036-45.

(21) Tang, T. H.; Bader, R. F. W.; MacDougall, P. J. *Inorg. Chem.* **1985**, *24*, 2047-53.

(22) Bachrach, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 6406. Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(23) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935-43.

(24) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872-4.

(25) Wiberg, K. B. *Inorg. Chem.*, in press.

(26) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; MacDougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142.

(27) Bader, R. F. W.; MacDougall, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 6788-95.

(28) Slee, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 7541-8.

(29) Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2499. Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81. Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, M., Eds.; Plenum Press: New York, 1982.

(30) McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comput. Chem.* **1985**, *9*, 165.

(31) Bachrach, S. M.; Streitwieser, A., Jr. *J. Comput. Chem.*, submitted for publication.

(32) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(33) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University Publication Unit, Pittsburgh, PA, 1983.

(34) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(35) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

Table III. Atomic Populations (Total Electrons) and Charge Change Accompanying Deprotonation

	Neutral Molecule						Anion						Charge Change					
Pop. Method	NPA			IBP			NPA			IBP			NPA			IBP		
Pop. Basis Set	3-21+G	6-31+G	6-31+G*	6-31+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G*	6-31+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G*	6-31+G	6-31+G	6-31+G*
Geom. Opt. BS	3-21+G	3-21+G	6-31(+)G*[a]	3-21+G	6-31G*	6-31(+)G*[a]	3-21+G	3-21+G	6-31(+)G*[a]	3-21+G	6-31G*	6-31(+)G*[a]	3-21+G	3-21+G	6-31(+)G*[a]	3-21+G	6-31G*	6-31(+)G*[a]
Formic Acid																		
C (1)	5.24	5.27	5.19	4.53	4.46	4.03	5.26	5.29	5.19	4.50	4.39	3.89	-0.02	-0.02	0.00	+0.03	+0.07	+0.14
H (2)	0.82	0.81	0.85	0.90	0.91	0.91	0.96	0.94	1.00	1.08	1.10	1.11	-0.14	-0.13	-0.15	-0.18	-0.19	-0.20
O (3)	8.67	8.65	8.69	9.09	9.13	9.39	8.89	8.88	8.90	9.21	9.26	9.50	-0.23	-0.24	-0.21	-0.12	-0.13	-0.11
O (4)	8.81	8.80	8.79	9.06	9.07	9.30	8.89	8.88	8.90	9.21	9.26	9.50	-0.08	-0.08	-0.11	-0.15	-0.19	-0.20
H (5)	0.46	0.47	0.48	0.43	0.44	0.37	-	-	-	-	-	-	+0.46	+0.47	+0.48	+0.43	+0.44	+0.37
Vinyl Alcohol																		
C (1)	5.81	5.82				5.57	5.71	5.72				5.31	+0.11	+0.11				+0.26
H (2)	0.77	0.77				0.94	0.90	0.89				1.10	-0.12	-0.12				-0.16
C (3)	6.59	6.59				6.01	6.85	6.85				6.26	-0.26	-0.26				-0.25
H (5)	0.76	0.76				0.97	0.82	0.82				1.08	-0.06	-0.06				-0.11
H (6)	0.78	0.78				1.00	0.81	0.80				1.06	-0.03	-0.03				-0.06
O (4)	8.79	8.79				9.05	8.92	8.93				9.20	-0.13	-0.13				-0.15
H (7)	0.49	0.49				0.46	-	-				-	+0.49	+0.49				+0.46
Ethanol																		
C (1)	6.10	6.10	6.04	5.49		5.33	6.06	6.07	5.95	5.37		4.94	+0.04	+0.03	+0.09	+0.12		+0.39
H (4,5)	0.80	0.80	0.82	1.03		1.03	0.89	0.88	0.93	1.13		1.16	-0.09	-0.08	-0.11	-0.10		-0.13
C (3)	6.69	6.70	6.66	5.89		5.91	6.70	6.70	6.66	5.95		5.99	-0.01	0.00	0.00	-0.06		-0.08
H (6)	0.77	0.77	0.78	1.03		1.02	0.83	0.83	0.84	1.11		1.11	-0.06	-0.06	-0.06	-0.08		-0.09
H (7,8)	0.76	0.75	0.77	1.00		1.00	0.79	0.79	0.81	1.06		1.06	-0.04	-0.04	-0.04	-0.06		-0.06
O (2)	8.82	8.83	8.82	9.03		9.25	9.04	9.06	9.05	9.17		9.49	-0.22	-0.23	-0.23	-0.14		-0.24
H (9)	0.50	0.50	0.51	0.49		0.41	-	-	-	-		-	+0.50	+0.50	+0.51	+0.49		+0.41

[a] 6-31+G* for formic acid and formate ion; 6-31G* for ethanol and ethoxide ion.

Accordingly, the 6-31G* structures were used for ethanol and ethoxide ion, but populations were calculated with diffuse functions added, e.g., 6-31+G*//6-31G*. Vinyl alcohol and its anion were calculated only at the 3-21+G level. The 3-21+G basis set is composed of the standard 3-21G basis set[37] to which a diffuse sp shell has been added. For comparison, the formic acid and ethanol systems were also calculated at this level. The 3-21+G optimizations differ significantly from the 6-31G* structures. The resulting structures are summarized in Table II.

Effect of Basis set and Population Analysis Method. NPA and IBP atomic populations for formic acid, formate ion, ethanol, and ethoxide ion were obtained with three different basis sets. IBP values were calculated with Bader's program;[38] natural populations were calculated with Weinhold's program.[39] The resulting populations are given in Table III. The corresponding atomic charges are summarized in Figure 1. It should be noted that for formic acid and formate ion the highest level populations are obtained at the 6-31+G*//6-31+G* level, but for ethanol and ethoxide ion they are obtained at the 6-31+G*//6-31G* level. We consider these two levels, which differ only in the presence or absence of added diffuse functions during the geometrical optimization, to be essentially equivalent.

There are significant basis set effects on electron density distributions and on the derived IBP's. The major variation arises from the inclusion or noninclusion of polarization functions. (Schweig[40] has shown that polarization functions are necessary to get good agreement between calculated and experimental electron densities.) For example, the carbonyl oxygen, O(3), IBP in formic acid is 9.346 at 3-21G*//3-21G*,[31] 9.387 at 6-

(36) Slee, T.; Larouche, A.; Bader, R. F. W. *J. Phys. Chem.*, submitted for publication.
(37) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(38) Biegler-Koenig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317. We are indebted to Professor Bader for a copy of his program.
(39) We thank Professor Weinhold for a copy of G82NPA.
(40) For a recent comprehensive review see: Breitenstein, M.; Dannöhl, H.; Meyer, H.; Schweig, A.; Seeger, R.; Seeger, U.; Zittlau, W. *Int. Rev. Phys. Chem.* **1983**, *3*, 335.

FORMIC ACID   ETHANOL

NEUTRAL MOLECULES
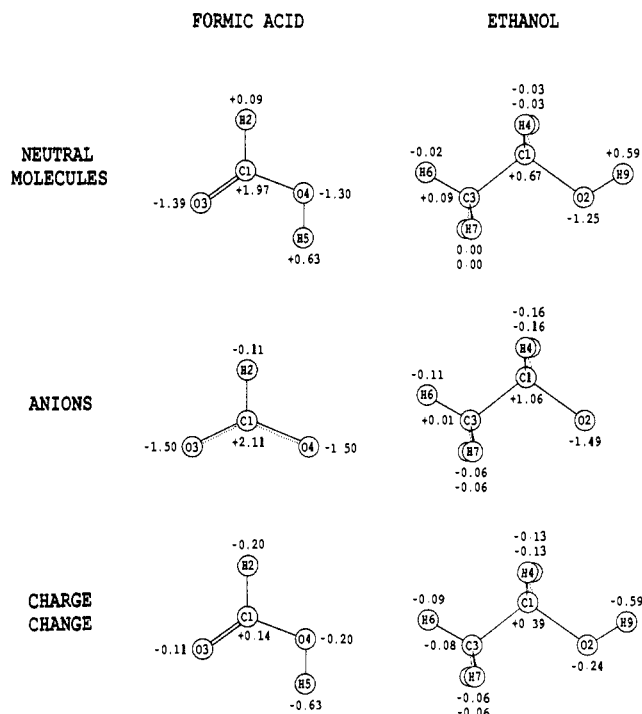
ANIONS

CHARGE CHANGE

Figure 1. Atomic charges and charge changes accompanying deprotonation. Values determined from integrated Bader populations using the 6-31+G* basis set.

31G*//6-31G*,[36] 9.389 at 6-31G**//6-31G*,[23] 9.39 at 6-31+-G*//6-31+G*, and 9.322 at 6-311G*//6-31G*.[36] However, if polarization functions are omitted, the result is significantly different, e.g., 9.13 at 6-31+G//6-31G*. The natural populations are much less sensitive to whether polarization functions are used. For example, the carbonyl oxygen, O(3), NPA of formic acid is 8.61 at 3-21G//3-21G,[31] 8.67 at 3-21+G/3-21+G, 8.65 at 3-21G*/3-21G*,[31] and 8.69 at 6-31+G*//6-31+G*. The following discussion of the electron populations and charges in the formic

Table IV. Group Populations (Total Electrons) and Charge Flow Accompanying Deprotonation

Pop Method	Neutral Molecule							Anion							Charge Change						
	NPA			IPP		IBP		NPA			IPP		IBP		NPA			IPP		IBP	
Pop Basis Set	3-21+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G*	6-31+G*	3-21+G	6-31+G	6-31+G*	3-21+G	6-31+G	6-31+G	6-31+G*
Geom Opt BS	3-21+G	3-21+G	6-31(+)G*	3-21+G	3-21+G	6-31G*	6-31(+)G*	3-21+G	3-21+G	6-31(+)G*	3-21+G	3-21+G	6-31G*	6-31(+)G*	3-21+G	3-21+G	6-31(+)G*	3-21+G	3-21+G	6-31G*	6-31(+)G*
Formic Acid																					
C(1) + H(2)	6 06	6 08	6 04	5 51	5 42	5 40	4 94	6 21	6 23	6 19	5.64	5 58	5 49	5 00	-0 16	-0 15	-0 15	-0 13	-0 16	-0 12	-0 06
O (3)	8 67	8 65	8 69	9 01	9 09	9 13	9 39	8 89	8 88	8 90	9.17	9 21	9 26	9 50	-0 23	-0 24	-0 21	-0 16	-0 12	-0 13	-0 11
O(4) + H(5)	9 27	9 27	9 27	9 46	9 49	9 51	9 67	8 89	8 88	8 90	9 17	9 21	9 26	9 50	-0 61	-0 61	-0 63	-0 71	-0 72	-0 75	-0 83
Vinyl Alcohol																					
C(1) + H(2)	6 59	6 59		6 62	6 51			6 60	6 61		6 36	6 41			-0 01	-0 01		+0 26	+0 10		
C(3) + H(5-6)	8 13	8 12		7 91	7 98			8 48	8 47		8 45	8 40			-0 35	-0 35		-0 54	-0 42		
O(4) + H(7)	9 28	9 28		9 46	9 51			8 92	8 93		9 17	9 20			-0 64	-0 64		-0 71	-0 69		
Ethanol																					
C(1) + H(4-5)	7 71	7 69	7 68	7 62	7 55		7 39	7 85	7 83	7 81	7 70	7.64		7 25	-0 14	-0 14	-0 13	-0 08	-0 09		+0 14
C(3) + H(6-8)	8 97	8 97	8 98	8 87	8 93		8 93	9 11	9 11	9 12	9 08	9 17		9 22	-0.14	-0 13	-0 14	-0 21	-0 24		-0 29
O(2) + H(9)	9 32	9 33	9 33	9 46	9 52		9 66	9 04	9 06	9 05	9 14	9 17		9 49	-0.72	-0 73	+0 28	-0 68	-0 65		-0 83

[a] 6-31+G* for formic acid and formate ion; 6-31G* for ethanol and ethoxide ion.

acid and ethanol systems will focus on IBP values at the highest level of theory used, 6-31+G*.

For comparison we have also determined populations using the IPP method at the 3-21+G//3-21+G level. However, because of limitations in the method, we were able only to determine group charges, where each group is defined as containing a second-row element and its attached hydrogens, if any. These results are given in Table IV together with the corresponding group populations obtained using the NPA and IBP methods for comparison. The IPP 3-21+G//3-21+G and IBP 6-31+G//3-21+G results are sufficiently similar that both lead to the same conclusions.

Natural populations differ markedly in absolute value from IBP's. NPA's predict lower bond polarities than IBP's for polar bonds such as C–O but yield higher polarities for relatively nonpolar bonds such as CH_3–H. The difference in many cases probably results from the feature that NPA is based on atom-centered basis functions and therefore automatically subtracts the effects of local atomic polarization. Different oxygens still show markedly little variation in NPA values. The increases in oxygen populations on deprotonation are relatively small and qualitatively comparable to the IBP changes. The carbons attached to oxygens are much less positively charged according to NPA and change less on deprotonation. The polarization changes at carbon on deprotonation are not discernible by NPA but the net charge transfer to peripheral hydrogens is comparable to the IBP results.

Total Populations and Charges. One of the most striking results apparent with the IBP 6-31+G* values in Table III is that the oxygen populations differ rather little among the neutral molecules and among the anions. This result holds true within a given basis set and confirms results reported elsewhere for a wider range of oxygen functionalities.[31] In formic acid, the carbonyl oxygen is more negative than the hydroxy oxygen, as suggested by resonance structure 1, but only by 0.09 electron. The hydroxy oxygen of formic acid is 0.05 more negative than that in ethanol while the acidic proton in formic acid is more positively charged (+0.63) than in ethanol (+0.59). The higher proton charge of formic acid is related to its higher acidity; the difference in oxygen charges affects the relative acidities in the opposite direction. Most striking are the charges on the anionic oxygens for formate and ethoxide ions upon deprotonation; they are virtually the same, -1.50 and -1.49, respectively. The total charge on oxygen in these anions, therefore, has no bearing on the relative basicity of the anions.

Another striking result is that the charges are large; all of the oxygen charges are more negative than -1. These charges are much greater than in conventional chemical thought, which derives mostly from the magnitudes of total dipole moments. It should be emphasized that the integrated electron populations are not centered on nuclei and the resulting net charges associated with the atoms-in-molecules (IBP's) are also associated with large atomic polarizations or local dipoles that generally offset effects of the large charges.[26,36] The electronegativity difference between

carbon and oxygen produces highly polar bonds, more so than has been traditionally recognized. All oxygens bonded to carbon and hydrogen have so much charge that there is little ability to attract additional charge. The polarity of such oxygen bonds is also demonstrated by the charges on their attached carbons. The charge on the central carbon in ethanol is +0.67 and in formic acid is +1.91. The carbon charges are even greater in the anions; in ethoxide the central-carbon charge is +1.06 and in formate it is +2.11. The greater cationic charge of the carbon in neutral formic acid provides electrostatic stabilization of the negative oxygens and is an important feature leading to the difference in acidity between alcohols and carboxylic acids. This is the electrostatic equivalent of the inductive effect argument presented above. The increased high positive charges on the central carbons of the anion can be understood as a consequence of polarization. Removal of the hydroxy proton increases the net negative charge at the hydroxy oxygen. This increased oxygen charge, in turn, polarizes electrons away from the attached carbon to the hydrogen and other oxygen in the case of formate, and to the hydrogens and methyl group in the case of ethoxide; the striking result is that the attached carbon is more positive in the anion than in the neutral molecule. A similar conclusion regarding the important role of polarization was reached by Wiberg in related systems.[24,25]

It is the electronegativity, or inductive effect, of the carbonyl oxygen that is responsible for the polarization of the carbonyl bond, and hence, for the highly charged central carbon atom that is found in formic acid compared to vinyl alcohol or ethanol. In effect, structure 2 is a dominant structure in the resonance picture of formic acid. This resonance structure is not generally considered

2   **3**   **4**
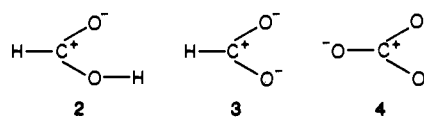
in the traditional view. Note that a dominant role for 2 requires that the short carbonyl bond distance be rationalized on the simple basis of electrostatic attraction of opposite charges. Structure 2 of formic acid is also that used in the Branch and Calvin treatment of the empirical inductive effect pK_a of formic acid (vide supra).

In the same manner, the IBP charges show that the best simple electronic structure for formate ion is that of a carbonium ion dioxide, **3**. Similarly, the IBP for the central carbon of carbonate ion is 3.30, indicative that the simple polar structure **4** is more important than structures containing C=O. Carbonate ion is an example of Y-conjugation that is the subject of a separate study.[41]

In ethanol, a greater amount of charge is transferred from the hydroxy group to the rest of the molecule during deprotonation

(41) Rajca, A., to be submitted.

Table V. Atomic π-Electron Populations and π-Charge Flow Accompanying Deprotonation

	Neutral Molecule				Anion				Charge Flow			
	NPA			IPP	NPA			IPP	NPA			IPP
	3-21+G	6-31+G	6-31+G*	3-21+G	3-21+G	6-31+G	6-31+G*	3-21+G	3-21+G	6-31+G	6-31+G*	3-21+G
	3-21+G	3-21+G	6-31+G*	3-21+G	3-21+G	3-21+G	6-31+G*	3-21+G	3-21+G	3-21+G	6-31+G*	3-21+G
Formic Acid												
C (1)	0.66	0.66	0.63	0.53	0.69	0.68	0.66	0.59	-0.03	-0.02	-0.03	-0.06
O (3)	1.46	1.46	1.49	1.56	1.66	1.66	1.66	1.71	-0.19	-0.20	-0.17	-0.15
O (4)	1.87	1.88	1.87	1.91	1.66	1.66	1.66	1.71	+0.22	+0.22	+0.21	+0.20
Vinyl Alcohol												
C (1)	0.93	0.93		0.94	0.81	0.81		0.78	+0.12	+0.12		+0.16
C (3)	1.15	1.14		1.10	1.47	1.46		1.43	-0.32	-0.32		-0.33
O (4)	1.92	1.93		1.96	1.72	1.73		1.79	+0.20	+0.20		+0.17

than in formic acid. This result is in keeping with the experimental and theoretical results of Siggel and Thomas[3] who found that the final-state relaxation effects in alcohols are slightly greater than in similar carboxylic acids. Most of the charge flowing from the hydroxy group goes to the methyl group (-0.24). The methyl group in ethanol is relatively neutral, and thus is able to accommodate more negative charge than the corresponding negative carbonyl oxygen in formic acid. This result is also consistent with the theoretical IBP analysis of Stutchbury and Cooper[42] who found that the hydrogens of the methyl group in ethanol act as a sink for electrons during ionization.

π and σ Electron Populations. The foregoing discussion applies to total atomic charges. A resonance structure such as **1** refers strictly to a π-electron effect, and there is no doubt that such π charge transfer occurs. An IPP treatment of a variety of substituted carbonyl groups showed that the expected π transfers occur, but that the net effect is diminished by back-polarization in the σ system.[43] The same phenomenon has been noted by Slee, Larouche, and Bader[36] in studies of π and σ effects on IBP values.

We have separated the π- and σ-electron populations using the NPA and IPP methods. The π-electron populations and π-charge flow accompanying deprotonation are given in Table V for formic acid and vinyl alcohol. The three sets of π populations given for each molecule and ion are in good agreement; the following discussion will use the IPP results.

The π-electron populations of the hydroxy-oxygen atoms in the two neutral molecules are somewhat less than the classical value of 2 and indicate conventional allylic-type π resonance. In formic acid, however, the carbonyl oxygen has 1.56 π electrons, and the carbonyl carbon has only 0.53; that is, the carbonyl group is strongly polarized in both the σ and π electronic systems. The group charge changes (total, π, and σ) accompanying deprotonation are given in Figure 2 for both IPP and NPA analyses. These charge changes are in good qualitative agreement. In comparing the two diagrams note that the IPP results pertain to CH and OH groups but that the NPA results are for individual atoms. The IPP results given in Figure 2a indicate that, within each group, the σ and π systems are reinforcing each other (either both gaining or losing electrons for a given group). On deprotonation, the hydroxy oxygen has a net gain of 0.32 σ electron and a loss of 0.21 π electron. The π electrons are lost mostly to the carbonyl oxygen via allylic resonance. The gain in σ electrons comes entirely from the exiting hydroxy proton and there is, in fact, a net flow of σ electrons from the hydroxy oxygen to the rest of the molecule. The carbonyl oxygen already has a high negative charge that is enhanced by the gain in π density and is therefore unable to accept much of the σ charge donated by the departing proton, which, instead flows to the remaining hydrogen. That is, in the absence of the π system, the σ electrons associated with the departing proton would have been expected (by analogy with the case of ethanol) to have been polarized to both the carbonyl oxygen and
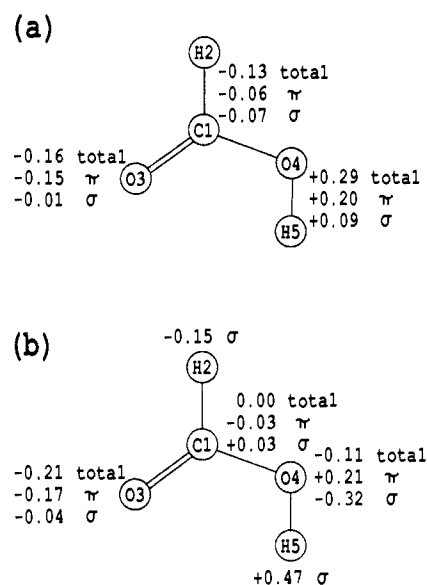

Figure 2. Charge change accompanying deprotonation of formic acid at the (a) IPP 3-21+G//3-21+G level using *group* populations and (b) NPA 6-31+G*//6-31+G* level using *atomic* populations.

the remaining hydrogen, but, because of the allylic π polarization, the net σ polarization is anisotropic and is primarily to the remaining hydrogen.

Vinyl Alcohol. Vinyl alcohol was chosen as a bridge between formic acid and ethanol. In the conventional interpretation, on deprotonation the anionic charge can be partially delocalized to the conjugated carbon, but such delocalization is less than in a carboxylate ion. We have, however, just shown by a multitude of methods that the higher acidity of carboxylic acids relative to alcohols is due to the highly polarized carbonyl group and not to differential charge rearrangement following deprotonation. Vinyl alcohol is of interest because it has the conjugation effects analogous to formic acid, but lacks the electronegativity effect of the carbonyl oxygen. Vinyl alcohol is predicted to have an acidity of 359.5 kcal mol⁻¹,[44] a value intermediate between formic acid and ethanol. This system therefore provides a valuable probe for the relative effects of conjugation and induction.

The geometry of vinyl alcohol and its anion were optimized at the RHF/3-21+G level with C_s symmetry imposed. Their conformations are analogous to those shown for formic acid and formate ion; all atoms, including the β-hydrogens, lie in a plane (see Figure 3). The optimized geometrical parameters are given in Table II.

We present a study of the charge distribution in vinyl alcohol and the charge changes that occur on deprotonation of vinyl

(42) Stutchbury, N. C. J.; Cooper, D. L. *J. Chem. Phys.* **1983**, *79*, 4967.
(43) Grier, D. L.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3556.

(44) Determined using the method described in: Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91.
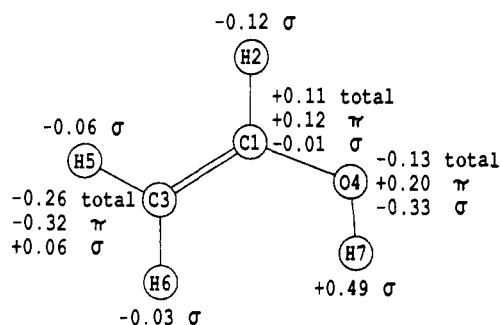
Figure 3. Charge change accompanying deprotonation of vinyl alcohol. Values determined using atomic populations from natural population analyses at the 6-31+G//3-21+G level.

alcohol for comparison with the above results on formic acid and ethanol; however, this work was done at a lower basis set level. Comparison of IBP values at 6-31+G//3-21+G with 6-31+-G*//6-31+G* or 6-31+G*//6-31G* of formic acid, ethanol, and their ions shows that the carbon–oxygen bond is less polarized in the small basis set but that qualitative changes on deprotonation are comparable. Interpretation of the small basis set results with vinyl alcohol are set in this context and are summarized in Table III together with the comparable basis set results of the other systems.

Inspection of the carbon populations given in Table III shows that the carbon–carbon double bond in vinyl alcohol is much more polarized than the carbon–carbon single bond in ethanol. This polarization is caused by the nearby negatively charged hydroxy oxygen. The effect of the polarization is to increase the polarization of the hydroxy bond and to make the potential at the hydroxy proton more positive. As a result, vinyl alcohol is a stronger acid than ethanol. A similar effect is seen in formic acid, where the highly polar carbonyl bond leads to a polarization of the hydroxy group in formic acid that is greater than that found in either vinyl alcohol or in ethanol.

In all three hydroxy groups, the changes in the hydroxy oxygen IBP at the 6-31+G//3-21+G level on deprotonation are comparable. There is an increase in the negative charge of the β carbon in vinyl alcohol, C(3), as suggested by enolic resonance *but there is a comparable increase in positive charge at the α* carbon, C(1). That is, the increase in positive charge at the α carbon is greater in vinyl alcohol than in ethanol or formic acid at the same basis set level. This suggests that polarization of the double bond is more important than enolic charge transfer. All of the vinyl hydrogens gain negative charge on deprotonation of vinyl alcohol, consistent with such polarization changes. This surprising result is clarified by dissection of π and σ electronic changes as summarized in Figure 3. On deprotonation, the hydroxy oxygen loses 0.2 π electron by charge transfer to the β

carbon, but this carbon also acquires 0.12 π electron from the α carbon by additional polarization of the double bond.

These results for vinyl alcohol can be summarized as follows: the mutual polarization of the carbon–carbon double bond and the O–H bond in the alcohol results in a hydroxy hydrogen more positive and more acidic than in ethanol but less so than in formic acid. On deprotonation, the increased charge on oxygen leads to greater polarization in the double bond and greater charge changes on carbon than in ethanol. Because this enhanced polarization is in the π system with some resultant back-σ polarization, the resultant σ polarization of charge to all of the attached hydrogens is actually less than in deprotonation of ethanol.

Conclusions

The argument used in most current textbooks that carboxylic acids are more acidic than alcohols primarily because of increased resonance stabilization of the carboxylate ion is not just oversimplified but is in error. Two different extrapolations from nonconjugated systems predict that the contribution of resonance toward the higher acidity of carboxylic acids is between about 2 and 5 kcal mol^{-1}, or about 6 to 16% of the acidity difference. Using an empirical equation suggested by Branch and Calvin,[12] approximately 80% of the acidity difference can be accounted for with carbonyl inductive effects. Analysis using integrated electron populations show that the OH groups are highly polarized and that this polarization is enhanced by the polarization or the polarizability of the rest of the molecule. Relative acidities of ethanol, vinyl alcohol, and formic acid can be interpreted qualitatively by these polarization effects that are already present in the acid. The polarization of the carbonyl group in formic acid is particularly pronounced. The results confirm the role of ground-state polarization on the acidities of other compounds deduced by Wiberg[24,25] and Thomas[45] and the general polarization effects recently summarized by Bader.[36] The best simple explanation for the enhanced acidity of carboxylic acids is the greater positive potential at the proton, which is influenced by the high positive charge at the carbonyl carbon; the same effect also stabilizes the carboxylate ion.

Atomic populations determined using the NPA, IPP, and IBP methods differ quantitatively from one another; however, the resulting electron flows accompanying deprotonation are in general qualitative agreement.

(45) Thomas, T. D. *Inorg. Chem.* **1988**, *27*, 1695.