

On the Relative Acidities of Organic Compounds: Electronic and Geometric Relaxation Energies

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Abstract: The energy for deprotonation of a molecule in the gas phase may be divided into an initial-state electrostatic part and a relaxation part. The electrostatic part is dominating in determining the relative acidities of organic compounds, but the relaxation part is not negligible. The relaxation energy may be split up in two parts, and accurate calculations (MP2/6-311++G**//RHF/6-311++G**) of these electronic and geometric relaxation energies are presented for 13 small organic molecules (four alkanes, three alcohols, two enols, and three carboxylic acids). It is shown that although the electronic relaxation energy is 2 orders of magnitude larger than the geometric relaxation energy, the difference in electronic relaxation energy and the difference in geometric relaxation energy between a pair of molecules may be of the same size. For example, while the electronic relaxation energy of the acetate anion is 6.1 kcal/mol smaller than that of the 2-propanoxide anion, the geometric relaxation energy is 4.6 kcal/mol larger. Hence, the two relaxation contributions partially cancel each other, and the total difference in deprotonation energy is approximately equal to the shift in initial-state electrostatic potential between the two compounds. The electronic relaxation energies are largest for the most easily polarizable molecules, and the geometric relaxation energies are largest for molecules where classical resonance arguments suggest strongly stabilized anions (carboxylic acids and enols). The MP2/6-311++G**//RHF/6-311++G** level of theory, including zero-point and thermal energy corrections, give computed absolute acidities, $\Delta H(298)$, very close to experimental gas-phase acidities (root-mean square deviation 1.1 kcal/mol).

Introduction

There are at least two factors that influence the relative acidities of organic compounds: resonance and electrostatic effects. As discussed by Wheland,¹ both these factors work to make carboxylic acids more acidic than aliphatic alcohols. The dipole moment of the carbonyl group makes the electrostatic potential at the site of the hydroxylic proton less negative in a carboxylic acid than in an alcohol, where this electrostatic effect is missing. Furthermore, a carboxylic acid and its anion are both stabilized by resonance, with the larger resonance energy for the carboxylate anion. Obviously, with an alcohol neither the neutral molecule nor the alkoxide anion has any significant resonance stabilization. Although Wheland concluded that “we cannot be sure how much of the observed effect must be attributed to each cause”,¹ the prevailing explanation has until recently been the latter one, that is, that resonance stabilization of carboxylate ions makes carboxylic acids more acidic than alcohols.²

Siggel and Thomas challenged this conventional view by comparing experimental gas-phase acidities with oxygen core-ionization energies and by quantum-chemical calculations.³ They explained the greater acidity of carboxylic acids relative to alcohols as principally due to electrostatic effects in the neutral

molecules: The highly polarized carbonyl group of a carboxylic acid gives a less negative, and hence less attractive, electrostatic potential for the acidic proton. Subsequent work in this area has fully or partially objected to⁴ and supported⁵ the explanation of Siggel and Thomas. For example, Wiberg^{4e} has found approximately half of the difference in acidity between ethanol and acetic acid to be due to the initial state charge distribution, and valence-bond calculations by Hiberty and Byrman^{4h} have shown that about half of the acidity difference between formic acid and ethanol comes from delocalization in the formate ion. In an empirical treatment of substituent effects Taft et al.^{4d} have found that the 33 kcal/mol difference in acidity between formic acid and ethanol to two-thirds depend on field effects and to one-third on resonance effects. Thus, it is still debated whether the high acidity of carboxylic acids can be fully explained without the argument of resonance. However, Siggel and Thomas³ clearly pointed out that resonance alone was not

(1) Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley & Sons: New York, 1955; pp 340–345.

(2) See, e.g., (a) Solomons, T. W. G. *Fundamentals of Organic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1986; p 666. (b) Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan Publishing Company: New York, 1992; p 486.

(3) Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360–4363.

(4) (a) Exner, O. *J. Org. Chem.* **1988**, *53*, 1810–1812. (b) Dewar, M. J. S.; Krull, K. L. *J. Chem. Soc., Chem. Commun.* **1990**, 333–334. (c) Godfrey, M. *Tetrahedron Lett.* **1990**, *31*, 5181–5184. (d) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047–2052. (e) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379–3385. (f) Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865–2868. (g) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1994**, *116*, 8885–8889. (h) Hiberty, P. C.; Byrman, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 9875–9880. (i) Neto, J. D. M.; Nascimento, M. A. C. *J. Phys. Chem.* **1996**, *100*, 15105–15110.

(5) (a) Siggel, M. R. F.; Streitwieser, A., Jr.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022–8028. (b) Thomas, T. D.; Carroll, T. X.; Siggel, M. R. F. *J. Org. Chem.* **1988**, *53*, 1812–1815. (c) Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A., Jr. *J. Mol. Struct. (THEOCHEM)* **1988**, *165*, 309–318. (d) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872–1874. (e) Ji, D.; Thomas, T. D. *J. Phys. Chem.* **1994**, *98*, 4301–4303. (f) Thomas, T. D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1945–1948. (g) Wiberg, K. B.; Ochterski, J.; Streitwieser, A. *J. Am. Chem. Soc.* **1996**, *118*, 8291–8299.

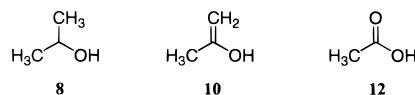
enough as explanation. Actually, in several recent textbooks on organic chemistry both the conventional (resonance) and the alternative (electrostatic or inductive) explanations for the acidity of carboxylic acids are discussed.⁶

Theoretical investigations of the relative acidities of alcohols and carboxylic acids have mainly been of four types: (I) Comparisons of calculated (and experimental) acidities for different types of compounds,^{4e,5a,7} (II) calculations of the electrostatic potential $V(H)$ at the acidic proton^{3,5e,f,8} or the "atomic energy" of that proton,^{4e} (III) direct evaluations of the resonance energy by valence bond methods,^{4h,i} and (IV) studies of the charge flow that follows upon deprotonation.^{4c,e,5a,c,g,7,8} One way of discussing the relative acidities of compounds is in terms of initial and final state effects. The conventional explanation for the acidity of carboxylic acids, that is, resonance in the carboxylate anion, then clearly focuses on the final state, whereas the alternative electrostatic explanation focuses on the initial state. Discussions based on charge flow calculations look at what happens to the electron distribution when going from the neutral molecule to the deprotonated anion. The common result of these studies is that the charge flow upon deprotonation is approximately the same for alcohols as for carboxylic acids, which indicates that differences in acidity should not depend on differences in charge flow, but on differences in the initial state potential. By definition, the charge flow reflects the relaxation of the electronic structure upon deprotonation, but how well it does so depends on the method with which the charge distribution is obtained. The best picture of the relaxation process is probably obtained by electron density difference maps.^{5c,g,7} However, charge flow calculations give no account of the energies involved in the relaxation process. Although many of the studies that have focused on the electrostatic potential $V(H)$ also reported relaxation energies, these were simply obtained as the difference between $-V(H)$ and the acidity (= the total energy change upon deprotonation).

For better understanding of the relaxation its energy may be divided into an electronic and a geometric part. The electronic relaxation energy ($R1$) is associated with the response of the electrons to the removal of the acidic proton (at fixed geometry), whereas the geometric relaxation energy ($R2$) is associated with the change in anion geometry from that of the neutral molecule to an optimal one. $R1$ is much larger than $R2$, and they are both smaller than $-V(H)$. (For example, for formic acid $-V(H) = 586$ kcal/mol (25 eV), $R1 = 227$ kcal/mol (10 eV), and $R2 = 8$ kcal/mol (0.3 eV).) To my knowledge, the only previous report of such relaxation energies in connection with the acidities of carboxylic acids, alcohols, or enols is in an Appendix by Siggel and Thomas,³ where unspecified values for $-V(H)$, $R1$, and $R2$ were given as 25–27, 9, and 0.1–0.6 eV, respectively. The calculations presented here are of a quality high enough to reproduce experimental gas-phase acidities to within 1–2 kcal/mol. Further, trends for the relaxation energies $R1$ and $R2$ and for the electrostatic potential $V(H)$ are discussed. This kind of analysis has also been applied to other systems: Speers et al. have investigated the deprotonation of dimethyl sulfide, dimethyl

sulfoxide, and dimethyl sulfone,⁹ and Laidig and Streitwieser have studied trends in acidity over the first and second period hydrides.¹⁰ Recently, Tupitsyn et al. reported on the investigation of CH acidity trends in monosubstituted methanes.¹¹

The change in electronic energy upon deprotonation is $\Delta E_{\text{elec}} = -V(H) - R1 - R2$ (vide infra) and with the numbers given above it is clear that $V(H)$ and $R1$ dominate the energy. When two compounds are compared the difference in energy change can be written as $\Delta\Delta E_{\text{elec}} = -\Delta V(H) - \Delta R1 - \Delta R2$ and in some cases, for example in a comparison of an alcohol with a carboxylic acid, the contributions $\Delta R1$ and $\Delta R2$ have different signs. Thus, although $-\Delta V(H)$ is always the dominant contribution to $\Delta\Delta E_{\text{elec}}$ when a comparison is made between compounds of different classes (e.g., alcohols and carboxylic acids), the partial cancellation of $\Delta R1$ and $\Delta R2$ in some cases leads to surprisingly small energy contributions from relaxation. In this paper 13 small molecules of four different classes are studied: four alkanes, four alcohols, three carboxylic acids, and two enols. Alcohols and carboxylic acids were chosen to contribute to the discussion of the greater acidity of carboxylic acids relative to alcohols. Enols (e.g., propen-2-ol, **10**) can be viewed as carboxylic acids with the oxygen atom of the carbonyl group exchanged for CH_2 . Thus, the double bond should still be available for resonance interactions, but it should be much less polar than in a carboxylic acid. Actually, although it was not experimentally verifiable,¹² Wheland considered enols to be typical examples of substances acidic due to resonance effects.¹ The alkanes were included in the investigation as nonpolar reference substances. They differ from the other three classes in that the "acidic" proton is bound to carbon instead of oxygen. The substances are chosen to be of similar shapes and sizes. For example, acetic acid (**12**) should be compared with 2-propanol (**8**) and propen-2-ol (**10**).



Computational Methods

The structures of all molecules and anions were geometry optimized at the RHF level with the 6-311++G** basis set.¹³ For molecules where preliminary 3-21G* calculations revealed several low-energy conformers, the geometry of each conformer was optimized at the RHF/6-311++G** level and only the conformer of lowest energy was considered in the further analysis. Single point energies and electrostatic potentials were then calculated at the MP2 level with the same basis set. The reported MP2 energies may thus be labeled as MP2/6-311++G**/RHF/6-311++G**. The zero-point energies and the thermal energy corrections from 0 to 298 K were obtained from calculations of vibrational frequencies at the RHF level, also with the 6-311++G** basis set. All ab initio calculations were performed with the program Gaussian98W,¹⁴ except the preliminary conformational searches which were done with the program Spartan.¹⁵ In all calculations standard basis sets internal to the programs were used.

(9) Speers, P.; Laidig, K. E.; Streitwieser, A. *J. Am. Chem. Soc.* **1994**, *116*, 9257–61.

(10) Laidig, K. E.; Streitwieser, A. *J. Comput. Chem.* **1996**, *17*, 1771–1781.

(11) Tupitsyn, I. F.; Popov, A. S.; Zatsypina, N. N. *Russ. J. Gen. Chem.* **1998**, *68*, 1314–1319.

(12) The equilibrium constant for the keto–enol tautomerism of acetone is approximately 6×10^{-9} in aqueous solution at 25 °C: Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460–462.

(13) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, *4*, 294–301.

(6) For example: (a) Solomons, T. W. G. *Organic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1996; pp 106–109. (b) Jones, M., Jr. *Organic Chemistry*; W. W. Norton & Company: New York, 1997; pp 958–959. (c) Bruice, P. Y. *Organic Chemistry*, 2nd ed.; Prentice Hall International, Inc.: Upper Saddle River, 1998; p 280. (d) Hart, H.; Craine, L. E.; Hart, D. J. *Organic Chemistry – A Short Course*, 10th ed.; Houghton Mifflin Company: Boston, 1999; p 289.

(7) Hadad, C. M.; Rablen, P. R.; Wiberg, K. B. *J. Org. Chem.* **1998**, *63*, 8668–8681.

(8) Siggel, M. R. F.; Thomas, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5795–5800.

Table 1. Energy Differences (kcal/mol) between Neutral Molecules and Anions^a

	ΔE_{elec}^b	$\Delta E(0)^c$	$\Delta E(298)^d$	$\Delta H(298)^e$	expt ^f
1 methane	427.4	416.6	417.6	418.1	418.0
2 ethane	429.8	418.6	419.5	420.1	420.1
3 propane	424.8	413.6	414.5	415.1	415.6
4 <i>iso</i> -butane	423.1	411.9	412.8	413.4	412.9
5 methanol	391.9	381.3	381.9	382.5	381.2
6 ethanol	387.6	377.2	377.8	378.4	378.0
7 1-propanol	386.9	376.4	377.1	377.7	376.2
8 2-propanol	385.1	374.7	375.4	376.0	375.7
9 vinyl alcohol	363.5	353.5	354.3	354.9	(355.1)
10 propen-2-ol	364.6	354.8	355.5	356.1	(354.2)
11 formic acid	350.8	341.5	342.3	342.9	345.3
12 acetic acid	354.8	345.5	346.3	346.9	348.1
13 propanoic acid	354.3	345.0	345.8	346.4	347.4

^a All energies are differences between anions and molecules, in kcal/mol. Absolute energies are given as Supporting Information. ^b $\Delta E_{\text{elec}} = E(\text{anion}) - E(\text{molecule})$ at the MP2/6-311++G**/RHF/6-311++G** level. ^c $\Delta E(0) = \Delta E_{\text{elec}} + \Delta ZPE$, where ZPE is the zero-potential energy correction (at the RHF/6-311++G** level). ^d $\Delta E(298) = \Delta E(0) + \Delta E(0 \rightarrow 298) + 3RT/2$, where $E(0 \rightarrow 298)$ is the thermal correction from 0 to 298 K (at the RHF/6-311++G** level) and $3RT/2$ corresponds to the translational energy of the proton. ^e $\Delta H(298) = \Delta E(298) + RT$, where RT is the pV-contribution due to one extra mole of gas after deprotonation. ^f Experimental gas-phase ΔH values were taken from the NIST Web site,¹⁹ except for entries 9 and 10, which are theoretical estimates from Rosenberg.²⁰ The experimental error bars are 2 kcal/mol or more.¹⁹

Energies

The calculated deprotonation energies (acidities) for 13 molecules are given in Table 1. In all 11 cases where experimental values are available, the calculated ΔH -values lie within 2 kcal of experiment, which is the same as the reported error bars of most of the experimental values. Seven of the calculated values have errors relative to experiment of 1 kcal/mol or less. Thus, the MP2/6-311++G**/RHF/6-311++G** level of theory, extended with RHF/6-311++G** zero-point and thermal energy corrections can reproduce experimental gas-phase acidities very accurately. Correlation of calculated and experimental $\Delta H(298)$ values for the 11 alkanes, alcohols, and carboxylic acids where experimental values are available gives a slope 1.018 ($R^2 = 0.9989$). The mean deviation of these 11 points is -0.1 kcal/mol (-0.004 eV), and the root mean square (rms) deviation is 1.1 kcal/mol (0.05 eV).¹⁶ These results show that this level of theory is as accurate as the computationally more expensive method MP4(SDTQ)/6-311++G(2d,p)/RHF/6-311++G(2d,p).¹⁸

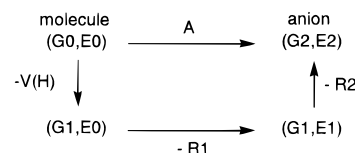
(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, 1998.

(15) *Spartan 5.1*; Wavefunction, Inc.; Irvine, 1998.

(16) These results were obtained without scaling of the vibrational frequencies prior to the thermochemical analysis. When instead a scale factor of 0.8929¹⁷ was used, the calculated $\Delta H(298)$ -values increased by 0.9–1.2 kcal/mol (see Supporting Information). This gave a slightly worse agreement with the experimental $\Delta H(298)$ -values (mean deviation +1.0 kcal/mol and rms deviation 1.5 kcal/mol). Since the thermochemical corrections do not enter into the following discussion of relaxation energies, the choice of scale factor is not crucial.

(17) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622–5629.

Scheme 1



Relaxation Contributions

Scheme 1 may be used as a starting point for discussing the various contributions to the energy of deprotonation. Here, G refers to geometries and E to electronic structures. G0 and G2 are the optimized geometries for the neutral molecule and the anion, respectively. G1, on the other hand, refers to the anion frozen in the geometry of the neutral molecule. E0 and E2 are the electronic structures (wave functions) of the neutral molecule and the anion, respectively. E1 is the electronic structure of the anion in the frozen geometry of the deprotonized molecule (G1).

With this scheme, the acidity, A, is defined as the difference in electronic energy between the neutral molecule and the anion. A then is positive, and the larger A is, the weaker acid is the molecule. $-V(H)$ is the negative of the electrostatic potential at the site of the acidic proton, which, after multiplication with the charge of the proton, is equal to the energy required to remove the acidic proton from the “frozen” molecule. When the electronic structure responds to the removal of the acidic proton ((G1,E0) \rightarrow (G1,E1)), the energy decreases ($R1 > 0$). R1 may be termed electronic relaxation energy, but it should be kept in mind that it only corresponds to that part of the relaxation that would take place in a hypothetical process with frozen geometry. In the final step of this cycle ((G1,E1) \rightarrow (G2,E2)), the geometry relaxes to that optimal for the anion, and R2, too, is positive. The same four states were considered by Siggel and Thomas,³ but in their following work they seem to only have used $V (= V(H))$ and $R (= R1 + R2)$.

The energies for (G0,E0) and (G2,E2) may obviously be obtained computationally by geometry optimizations of the molecule and the anion, respectively. The energy of (G1,E1) may be obtained through a single-point energy calculation after removal of the acidic proton. Finally, the energy of (G1,E0) may be obtained indirectly by a calculation of $V(H)$ for the (G0,-E0) state. At the RHF level of theory the energy of (G1,E0) may alternatively be calculated in a non-SCF fashion, that is, by removal of the proton from G0 to get G1, and then evaluation of the energy without reoptimization of the wave function.

The change in electronic energy for the deprotonation, ΔE_{elec} , is

$$\begin{aligned} \Delta E_{\text{elec}} &= E_{\text{elec}}(\text{anion}) - E_{\text{elec}}(\text{molecule}) = \\ &E(G2,E2) - E(G0,E0) = \\ &[E(G2,E2) - E(G1,E1)] + [E(G1,E1) - \\ &E(G1,E0)] + [E(G1,E0) - E(G0,E0)] = \\ &\quad - R2 - R1 - V(H) \quad (1) \end{aligned}$$

Thus, if the acidity to a first approximation is taken as the change in electronic energy, the difference in acidity between two compounds, ΔA , may be broken up in three parts:

$$\Delta A = \Delta \Delta E_{\text{elec}} = -\Delta V(H) - \Delta R1 - \Delta R2 \quad (2)$$

The energy contributions $-V(H)$, R1 and R2 from Scheme 1 are listed in Table 2 for the 13 substances of this investigation.

(18) Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91–96.

Table 2. Energy Contributions (kcal/mol) to the Enthalpy Change for Deprotonation^a

		$-V(H)^b$	$R1^c$	$R2^c$	$\Delta E_{\text{thermal}}^d$	$\Delta H(298)^e$
1	methane	700.6	272.8	0.4	-9.2	418.1
2	ethane	704.7	273.5	1.4	-9.7	420.1
3	propane	703.6	277.4	1.4	-9.7	415.1
4	<i>iso</i> -butane	702.9	278.3	1.5	-9.7	413.4
5	methanol	624.4	228.5	4.0	-9.4	382.5
6	ethanol	624.4	233.0	3.9	-9.2	378.4
7	1-propanol	624.4	233.6	3.9	-9.2	377.7
8	2-propanol	624.8	235.6	4.1	-9.1	376.0
9	vinyl alcohol	603.9	234.4	6.0	-8.6	354.9
10	propen-2-ol	606.9	235.9	6.4	-8.5	356.1
11	formic acid	585.8	227.3	7.7	-7.9	342.9
12	acetic acid	593.1	229.6	8.7	-7.9	346.9
13	propanoic acid	594.1	230.9	8.8	-8.0	346.4

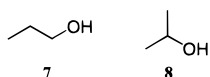
^a All energies are in kcal/mol and calculated from Table 1. ^b $V(H)$ = electrostatic potential at the acidic proton site in the neutral molecule, multiplied with proton charge. ^c $R1$ and $R2$ are relaxation energies defined in Scheme 1. ^d $\Delta E_{\text{thermal}}$ is the difference in thermochemical corrections from ΔE_{elec} to $\Delta H(298\text{ K})$, i.e., $\Delta ZPE + \Delta E(0 \rightarrow 298) + 5RT/2$, see Table 1. ^e $\Delta H(298) = \Delta E_{\text{elec}} + \Delta E_{\text{thermal}} = -V(H) - R1 - R2 + \Delta E_{\text{thermal}}$.

As seen above, to get quantum-chemical calculations of the acidity to approach experimental gas-phase ΔH values, contributions from zero-point energies, thermal corrections, and pV work are also needed. These are also listed in Table 2, grouped together as $\Delta E_{\text{thermal}}$ (i.e., $\Delta E_{\text{thermal}} = \Delta ZPE + \Delta E(0 \rightarrow 298) + 5RT/2$, where ΔZPE is dominating.)

Discussion

From Table 2 it is clear that the initial state electrostatic potential $V(H)$ is about three times as large as the relaxation energy $-(R1+R2)$. This is in line with the reasoning of Siggel and Thomas.³ The same result was obtained for quite different systems by Speers et al.,⁹ Laidig and Streitwieser,¹⁰ and Tupitsyn et al.¹¹ A closer look at the data in Table 2 reveals that the initial state electrostatic potential at the site of the acidic proton, $V(H)$, is distinctly different for the four classes of compounds. I.e., for the alcohols $-V(H)$ is 624–625 kcal/mol, which is smaller than $-V(H)$ for the alkanes but larger than $-V(H)$ for the enols or the carboxylic acids. This is as expected, and reflects the charge distribution within the molecules. Carboxylic acids have strongly polarized carbonyl groups, leading to relatively small values for $-V(H)$, and relatively weakly bound hydroxyl protons. The enols, too, have smaller values for $-V(H)$ than the alcohols (vide infra). It is interesting that whereas $-V(H)$ increase with molecular size for enols and carboxylic acids, there is almost no variation of $-V(H)$ among the alcohols.

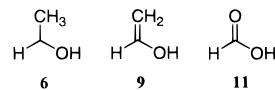
The electronic relaxation energies $R1$ also follow distinct trends. As expected this relaxation energy is larger the larger the molecule is. For example, $R1$ increases in both of the series methanol–ethanol–propanol and formic acid–acetic acid–propanoic acid due to the growing alkyl chains. $R1$ is also larger for 2-propanol (**8**) than for 1-propanol (**7**) due to the closer proximity of the methyl groups to the anionic center in the former. Hence, alkyl groups clearly increase the electronic relaxation energy $R1$. Since alkyl groups conventionally are thought of as electron-releasing, they could in principle destabilize a forming negative charge in the anion. Clearly, it is their ability of being easily polarized that is most important here.



Comparing the electronic relaxation energy $R1$ between different classes, we find that it is largest for the most polarizable molecules, the alkanes. The carboxylic acids, with the most strongly bound valence electrons have the smallest polarizabilities²¹ and also slightly lower $R1$ values than alcohols and enols.²²

The geometric relaxation energies $R2$ are much smaller than the electronic relaxation energies $R1$. There are, however, evident differences in $R2$ between alkanes, alcohols, enols and carboxylic acids. The two classes of molecules where resonance in the anions is supposed to be important, that is, carboxylic acids and enols, have higher geometric relaxation energies than the other two classes. Since resonance stabilization will have both electronic and geometric contributions, there is, however, no direct connection between $R2$ and the amount of resonance stabilization. It is also possible to imagine that there might exist anions with no resonance stabilization but with large geometric relaxation energies due to steric effects. Thus, the analysis presented here merely suggests that $R2$ is large for those anions where classical resonance arguments predict large resonance stabilization, not that $R2$ is a measure of the resonance stabilization.

In Table 3 direct pairwise comparisons of compounds of similar size and shape are listed, for example, formic acid (**11**) and ethanol (**6**), or formic acid (**11**) and vinyl alcohol (**9**). Although the calculated absolute acidities are quite accurate (see Table 1), the relative errors in the $\Delta H(298)$ values, that is, in the calculated shifts in $\Delta H(298)$, may be rather large.²³ However, these shift values are accurate enough for a discussion of trends between different substances.



As suggested by Siggel and Thomas,³ it is the initial state electrostatic potential which determines that the carboxylic acids are more acidic than the alcohols: $-V(H)$ is 39 kcal/mol lower for formic acid than for ethanol (Table 3, entry a), and 32 kcal/mol lower for acetic acid than for 2-propanol (entry b). Something new may, however, be extracted from Table 3, namely that the electronic and geometric relaxation sometimes work in opposite directions. Whereas the electronic relaxation energy $R1$ is larger for ethanol (more polarizable than formic acid), the geometric relaxation energy $R2$ is larger for formic acid (where resonance in the carboxylate anion is possible). The effect is the same for the pair acetic acid and 2-propanol. For cases such as these, when $-\Delta R1$ and $-\Delta R2$ almost cancel each other, the experimental difference in gas-phase acidity will be approximately equal to $-\Delta V(H)$. One might then say that the

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(21) Average electric dipole polarizabilities (in units of 10^{-24} cm^3) for molecules of similar size: propane 6.37 – ethanol 5.11 – formic acid 3.4 and *iso*-butane 8.14 – 2-propanol 6.97 – acetic acid 5.1 (Miller, T. M. *Atomic and Molecular Polarizabilities*. In *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995; pp 10/198–10/206).

(22) For the enols experimental polarizabilities are not available, but calculated polarizabilities (RHF/6-311++G**, see Supporting Information) are very similar to those of the alcohols: vinyl alcohol 4.17 – ethanol 4.20 and 2-propenol 5.86 – 2-propanol 5.89. (For the 11 alkanes, alcohols and carboxylic acids calculated polarizabilities correlate well with experimental ($R^2=0.9973$)).

(23) The relative errors ($(|\text{calculated} - \text{experimental}|/|\text{experimental}|)$) in $\Delta H(298)$ for entries a, c, and e of Table 3 are 0.08, 0.02, and 0.23, respectively.

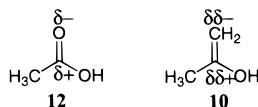
Table 3. Pairwise Comparisons of Energy Contributions (kcal/mol) to the Differences in $\Delta H(298\text{ K})$ for Deprotonation^a

		$-\Delta V(\text{H})$	$-\Delta R1$	$-\Delta R2$	$\Delta\Delta E_{\text{thermal}}$	$\Delta\Delta H(298)$
a	formic acid (11)–ethanol (6)	−38.6	5.6	−3.8	1.3	−35.5
b	acetic acid (12)–2-propanol (8)	−31.7	6.1	−4.6	1.2	−29.0
c	vinyl alcohol (9)–ethanol (6)	−20.5	−1.4	−2.1	0.6	−23.5
d	propen-2-ol (10)–2-propanol (8)	−17.9	−0.2	−2.4	0.7	−19.8
e	formic acid (11)–vinyl alcohol (9)	−18.1	7.1	−1.7	0.6	−12.0
f	acetic acid (12)–propen-2-ol (10)	−13.8	6.3	−2.3	0.6	−9.2
g	propane (3)–ethanol (6)	79.2	−44.5	2.5	−0.5	36.7

^a All energy differences are in kcal/mol. $\Delta\Delta H(298) = -\Delta V(\text{H}) - \Delta R1 - \Delta R2 + \Delta\Delta E_{\text{thermal}}$. For further explanations, see Table 2.

effect of the electrostatic potential is of an “anomalously” large importance. If we, for example, compare propane and ethanol (entry g of Table 3), $-\Delta R1$ cancels half of $-\Delta V(\text{H})$, and it is obvious that there must be more than one important energy contribution to $\Delta\Delta H(298)$.

When we compare the alcohols with the relevant enols, it should be possible to see the effect of the carbon–carbon double bond. The pairs vinyl alcohol (9)–ethanol (6) and propen-2-ol (10)–2-propanol (8) are listed in Table 3 (entries c and d). Obviously the double bonds of the enols are polarized to give less negative potentials at the acidic protons (less strongly bound protons). This effect is similar to the polarization of the carbonyl bond in the carboxylic acids, but is smaller in magnitude.



Precisely as the carboxylic acids, the enols have larger geometric relaxation energies $R2$ than the corresponding alcohols. However, the electronic relaxation energies $R1$ are similar for enols and alcohols. This is in line with the similar polarizabilities for alcohols and enols of similar size.

Thus, when a carboxylic acid is compared to the corresponding enol (Table 3, entries e and f), the acid has a less attractive initial state electrostatic potential for the proton, but this is substantially counteracted by the larger electronic relaxation energy $R1$ of the enol. Finally, the carboxylic acid has a somewhat larger geometric relaxation energy $R2$ than the enol.

An effect similar to that reported here may be detected also in the work of Speers et al. on the CH acidity of sulfur-containing substances.⁹ Their Scheme 1 contains the three energy contributions to deprotonation, and for the pair dimethyl sulfoxide–dimethyl sulfide $-\Delta V(\text{H}) = -25.9$, $-\Delta R1 = +13.8$, and $-\Delta R2 = -8.2$ kcal/mol may be calculated. Hence, dimethyl sulfoxide, which may be supposed to have an anion considerably stabilized by resonance, has a relatively large geometric relaxation energy, and as a consequence $-\Delta R1$ and $-\Delta R2$ partially cancel. Tupitsyn et al., too, found largest geometric relaxation energies for molecules with resonance stabilized anions, viz. acetaldehyde ($R2 = 25$ kcal/mol) and nitromethane, ($R2 = 44$ kcal/mol).¹¹

If $V(\text{H})$ reflects how “distorted” the electron distribution in a molecule is relative to a nonpolar alkane of similar size and shape, and if $R1$ reflects how well this electron distribution can respond to some change in the molecule, viz. the removal of a proton, then it may be assumed that there could be a close relationship between the two of them. Figure 1 shows a plot of $R1$ as a function of $-V(\text{H})$ for the 13 substances of this investigation. The broken line is a least-squares fit to the data points for the enols and the carboxylic acids only. The alkanes clearly accord very well with an extrapolation of this fit while the alcohols lie quite off the line. The alcohols are further distinguished by a nearly constant initial state electrostatic

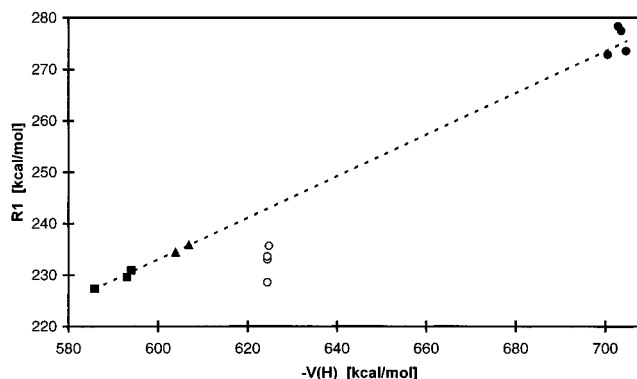


Figure 1. Electronic relaxation energies $R1$ as a function of initial state electrostatic potentials $-V(\text{H})$. All data are in kcal/mol and taken from Table 2: alkanes (●), alcohols (○), enols (▲), and carboxylic acids (■). The broken line is a linear least-squares fit to the five leftmost data points, i.e., to the carboxylic acids and the enols ($R^2 = 0.9898$, slope = 0.406, intercept = -10.7).

potential $V(\text{H})$. Except for the alcohols, a decreasing initial state electrostatic potential (more negative $V(\text{H})$, weaker acid) is accompanied by an increasing electronic relaxation energy (stronger acid). The slope of this correlation is, however, much smaller than unity, and the substances to the right in the diagram are the less acidic. Similar correlations may also be made with some of the data of the previous work on deprotonations.²⁴

The group of the four alcohols is unique in that all have approximately the same initial state electrostatic potential $V(\text{H})$ at the acidic proton and also approximately the same geometric relaxation energy $R2$, see Table 2. Thus, both the electrostatic potential and the geometric relaxation energy are local effects, and the difference in acidity between aliphatic alcohols of different sizes solely depend on different electronic relaxation energies $R1$. This is in accord with the reasoning of Taft et al.²⁵ that the effect of alkyl substituents on the experimental gas-phase acidities of alcohols is dominated by stabilizing charge-induced polarization of the alkyl substituents, rather than destabilizing inductive electron-releasing effects. Larger alkyl groups on the alcohols are more easily polarized which leads to larger electronic relaxation energies $R1$.

Conclusions

The absolute acidities for 13 small organic molecules (alkanes, alcohols, enols, and carboxylic acids) have been calculated at the MP2/6-311++G**//RHF/6-311++G** level

(24) The three sulfur-containing CH acids of Speers et al.⁹ (calculated at the RHF/6-31++G** level) fit quite well to the correlation line of Figure 1. This is probably a coincidence, as the five second period hydrides of Laidig and Streitwieser¹⁰ (also RHF/6-31++G**) lie well above the correlation line while the three heaviest of the first period hydrides lie well below the line. Common to all three of these series is, however, that $R1$ increases when $-V(\text{H})$ increases.

(25) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wolf, J. F.; DeFrees, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765–7767.

of theory. The theoretical data correlate very well with experimental gas-phase acidities. For those 11 substances where experimental ΔH -values are available computed acidities lie within 2 kcal/mol of the experiments, and the rms error is only 1.1 kcal/mol (0.05 eV).

As suggested by Siggel and Thomas,³ it is the initial-state electrostatic potential that makes carboxylic acids more acidic than aliphatic alcohols. The relaxation energy may be split up into two terms, associated with electronic and geometric relaxation of the anion after removal of the acidic proton. The electronic relaxation energy is approximately 2 orders of magnitude larger than the geometric relaxation energy, but when two substances are compared, the differences in these two energies may be of similar size. When a carboxylic acid is compared with an alcohol, the electronic relaxation favors deprotonation of the alcohol, while the geometric relaxation favors deprotonation of the carboxylic acid, and the two relaxation energies almost cancel each other. Thus, not only is the shift in initial state potential between the neutral molecules larger than the shifts in the two relaxation energies, but it becomes totally dominating because of the small sum of the two counteracting relaxation contributions.

Generally, the electronic relaxation energies are largest for the alkanes, which are easily polarizable molecules. The carboxylic acid molecules have relatively strongly bound valence electrons. They are the least polarizable molecules of this study,

and they have the smallest electronic relaxation energies. The geometric relaxation energies are largest for those two classes of substances where conventional theory says that resonance of the anions is important, that is, for the carboxylic acids and the enols. Thus, when an enol and an alcohol are compared (e.g., propen-2-ol and 2-propanol), both the geometric relaxation energy and the initial state electrostatic potential work to make the enol more acidic.

Of the four classes of molecules the alcohols stick out as having local effects determining both the electrostatic potential at the acidic proton and the geometric relaxation energy. The increase in acidity for larger alcohols is due to an increase in the electronic relaxation energy, which in turn depends on the polarizability of alkyl groups.

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Supporting Information Available: Cartesian coordinates for optimized geometries, absolute energies, electrostatic potentials, polarizabilities, and zero-point and thermal energy corrections for **1–13** (ASCII and PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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