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# Acidities of Nitric and Nitrous Acids

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It is shown from ab initio calculation of relevant energies that the greater acidity of nitric acid relative to nitrous acid and the greater acidities of these acids relative to common organic acids are due to the initial-state charge distribution in the molecules and not to preferential resonance stabilization of negative charge in the anions. The results presented are in accord with those obtained by Wiberg from charge density maps for the acids and their anions but provide a more quantitative insight into the contributions of these effects to the relative acidities.

The acidity of carboxylic acids and phenols is often attributed to the stabilization of the anion because of resonance delocalization of the negative charge that remains after the proton is removed.[1] It has, however, been shown by Siggel and Thomas[2] that such resonance delocalization in the anion plays little role in determining the difference in acidity between either carboxylic acids or phenol, where resonance is possible, and alcohols, where it is not. Rather, the difference is due to the charge distribution in the neutral molecule, which establishes a potential at the hydroxyl hydrogen in the acids that is more positive than that in the alcohols. Because of this more positive potential, it is easier to remove the hydroxyl proton from a carboxylic acid than from an alcohol. This view has been supported by calculations reported by Thomas, Siggel, and Streitwieser[3] and by Wiberg and Laidig.[4] These deal with the charge density in formic acid, acetic acid, and ethanol and the charge flow that occurs in these species when the hydroxyl proton is removed.

A similar question can be asked about such oxo acids as nitric acid and nitrous acid, where there is also the possibility for resonance delocalization of the $\pi$ electrons in the anion. For nitric acid there are three equivalent resonance forms of the anion, and for nitrous acid there are two. One might, therefore, expect that stabilization of the anions contributes to the acidity of these molecules and that preferential stabilization of the nitrate ion could account for the greater acidity of nitric acid. An alternate view, in keeping with the picture developed by Siggel and Thomas for carboxylic acids, is that the acidity of these acids results from the charge distribution in the neutral molecule. Two factors affect this charge distribution. These are the inherent electronegativity of oxygen and the possibility of resonance delocalization of electrons from the hydroxyl oxygen to the other oxygens. Both of these will contribute to the acidity of these molecules and to the greater acidity of nitric acid. In nitric acid, there are three oxygen atoms competing to withdraw charge from the central nitrogen whereas in nitrous acid there are only two. In nitric acid, the hydroxyl oxygen will, therefore, be less negative than in nitrous acid and will attract the proton less strongly.

The effect of resonance in the neutral species is illustrated in structures I–III. For nitric acid, two structures that put positive

$$\underset{\mathrm{I}}{\mathrm{H{-}O{-}N{=}O}} \qquad \underset{\mathrm{II}}{\mathrm{H{-}O^{+}{=}N{-}O^{-}}} \qquad \underset{\mathrm{III}}{\mathrm{H{-}O{-}N^{+}{-}O^{-}}}$$

charge on the hydroxyl oxygen and two that put positive charge on the nitrogen can be drawn. These structures lead to a more positive potential at the hydrogen in nitric acid and, hence, contribute to the stronger acidity of nitric acid.

An analysis by Branch and Calvin[5] shows that the acidity of nitrous acid in solution can be approximately accounted for by considering only inductive effects. In detail, however, their predicted p$K$ for nitrous acid is higher than observed by 2.3 p$K$ units. They attribute this difference to resonance effects, although it is not clear as to whether the resonance effect is on the initial state through structures such as II and III or on the final state through delocalization of the charge over equivalent species.

Calculations by Wiberg[6] show that both the electronegativity of oxygen and structures such as II contribute to the charge distribution in nitric and nitrous acids. Furthermore, since the nitrogen in nitrous acid is calculated to have less than one $\pi$ electron, there must be contributions from III to this molecule. By comparing charge distributions in the anions with those in the neutral molecules, Wiberg has concluded that charge flow after ionization is small. On the basis of these results, he states that "the traditional resonance depiction of these molecules does not fit well with the charge distribution found by using extended basis set ab initio calculations. The acidity of these acids is largely determined by the ground-state charge polarization caused by the difference in electronegativity between oxygen and nitrogen."

Although Wiberg's calculations are consistent with this conclusion, they do not provide any measure of the quantitative contributions to the acidities of the ground-state polarization (or, more generally, the ground-state charge distribution) and the changes in electron population on ionization (relaxation). In particular, although Wiberg concludes that there is little contribution from electronic relaxation to the acidity of these molecules, his calculations show that about one-fourth of a $\pi$ electron is transferred from the hydroxyl oxygen to the other oxygens when the proton is removed. Although this is only half of what would be expected from a traditional picture, it is not necessarily negligible.

The quantitative question of the relative contributions to the acidity of the initial-state charge distribution and the final-state relaxation is not answered by consideration of the charge distribution alone. Such information is, however, easily obtained from calculations of the sort described by Siggel and Thomas.[2] The acidity, $A$, which is the difference between the energy of the anion and that of the neutral molecule, is given by

$$A = -V - R \tag{1}$$

where $V$ is the potential energy of the acidic proton and $R$ is the change in energy of the anion that results when the electrons and nuclei adjust to the disappearance of the proton. $V$ depends on the initial-state charge distribution; $R$ depends on the charge flow when a proton is removed and includes the effects of resonance stabilization of the anion. $V$ can be determined directly from the wave functions from an electronic structure calculation for the molecule. $R$ is found most easily by determining $A$ from the calculated total energies for the neutral molecule and the anion. This is combined with the value of $V$ using (1) to give $R$.

To investigate the importance of these two effects on the relative acidities of nitric and nitrous acids, I have done such calculations, using the Gaussian-82 program[7] and the 3–21+G basis set[8] at

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[1] Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed; Allyn and Bacon: Boston, MA, 1987; p 836.

[2] Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360.

[3] Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A., Jr. *J. Mol. Struct. THEOCHEM*, in press.

[4] Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.*, in press.

[5] Branch, G. E. K.; Calvin, M. *The Theory of Organic Chemistry*; Prentice-Hall: New York, 1941; p 201.

[6] Wiberg, K. B., submitted for publication in *Inorganic Chemistry*.

[7] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. "Gaussian 82"; Carnegie-Mellon University Publication Unit: Pittsburgh, PA, 1983.

[8] Clark, T.; Chandrasekhar, J.; Spitznagel, G.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

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**Table I.** Calculated Acidities, Potential Energies, and Relaxation Energies for Different Acids (eV)

| | acidity[a] (*A*) | potential energy[b] (*V*) | relaxation energy (*R*) |
|---|---|---|---|
| nitric acid | 13.34 | −22.65 | 9.31 |
| nitrous acid | 14.47 | −24.18 | 9.71 trans |
| | 14.43 | −23.91 | 9.48 cis |
| formic acid | 14.93 | −24.25 | 9.32 |
| acetic acid | 15.12 | −24.63 | 9.51 |
| 2-propanol | 16.83 | −26.35 | 9.52 |
| nitric minus nitrous | −1.13 | 1.53 | −0.40 trans |
| | −1.09 | 1.26 | −0.17 cis |

[a] This work for nitric and nitrous acids; ref 11 for others. [b] This work for nitric and nitrous acids; ref 13 for others.

the RHF level. Geometries of all species were optimized at this level. For nitrous acid, calculations were done for both the cis and trans forms. In agreement with experiment,[9] the trans form is slightly lower in energy.[10] The relevant results of these calculations are summarized in Table I, together with those for other acids for comparison. The last two rows of this table show the differences between the calculated quantities for the two nitrogen acids. It is apparent from these results that the principal factor affecting the relative acidity of these two species is the initial-state potential, and, hence the ground-state charge distribution (or polarization of the charge density). Furthermore, final-state relaxation appears to favor the acidity of the weaker acid, nitrous acid. Thus, resonance delocalization in the anion does not play a role in the higher acidity of nitric acid.

The discussion above deals with the acidities of nitrous and nitric acids relative to each other. It is also useful to inquire into their acidity relative to other common acids. As noted above, the analysis by Branch and Calvin[5] shows that the acidity of nitrous acid is largely accounted for by inductive effects, which arise from the electronegativity of the oxygen. In detail, however, their work shows that there is a significant contribution to the acid strength from resonance, either in the neutral molecule or in the anion. For such a comparison, Table I shows the calculated acidities,[11] initial-state potentials,[2] and final-state relaxation energies for acetic acid and 2-propanol. These are chosen because they have the same number of second-row atoms as nitric acid, so that effects having to do simply with the size of the molecule will be nearly constant. Acetic acid provides an example where resonance may contribute to the acidity;[12] 2-propanol provides one where resonance does not. We see that the wide range of acidities encompassed by these molecules, 3.5 eV, is accounted for almost entirely by the initial-state potential, which covers a comparable range of 3.7 eV. The spread in relaxation energies is, however, only 0.4 eV.

Although the role of the initial-state potential is clear from these results, one cannot decide from these alone whether resonance structures such as II and III contribute to this potential. However, the analysis by Branch and Calvin[5] indicates that there is a resonance contribution to the acidity of nitrous acid. From the discussion presented here, this must be in the initial state. Furthermore, the charge distribution presented by Wiberg also indicates some contributions of II and III to the structure. Thus it is reasonable to conclude that there is an initial-state resonance contribution to the acidity of nitrous acid. The situation for nitric acid is less clear. Since it is a strong acid, it was not included in the analysis made by Branch and Calvin. Wiberg's charge densities show that the $\pi$ populations are 1.00 on nitrogen, 1.9 on the hydroxyl oxygen, and 1.5–1.6 on the other oxygens. These are very close to the values of 1, 2, and 1.5 that one would expect for a structure without resonance contributions.

Finally, it is of interest to compare nitrous acid with formic acid, since these acids have similar structures and are isoelectronic. They differ in acidity by less than 0.5 eV. The appropriate energies for formic acid[11,13] are included in Table I. Since formic acid exists in the cis form it is most instructive to compare the formic acid results with those for *cis*-nitrous acid. In this comparison we see a result that is not surprising. The higher acidity of nitrous acid arises primarily from the shift in initial-state potential (0.34 eV), reflecting the higher electronegativity of nitrogen relative to carbon. The contribution of relaxation to the relative acidities is only half as great. If, however, we compare the data with those for the *trans* isomer of nitrous acid, we come to the opposite conclusion. The difference between nitrous and formic acids in this case is primarily due to relaxation. As the hydrogen atom is rotated from the cis to the trans position, there is rearrangement of electron density in such a way as to affect the potential at the hydrogen atom, without significantly affecting the total energy of the molecule.

In summary, the acidities of nitric acid and nitrous acid relative to each other and relative to two other common acids are determined almost entirely by the initial-state charge distribution and not by differences in the stabilization energies of the anions. Resonance forms such as II and III probably contribute to the charge distribution in nitrous acid; the situation is less clear for nitric acid. These results are in accord with the conclusions reached by Wiberg. However, the approach presented here gives a more quantitative picture of the influence of the initial- and final-state effects on acidity than can be obtained from inspection of charge-density maps or atomic charges.

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**Registry No.** Nitric acid, 7697-37-2; nitrous acid, 7782-77-6.

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(9) Jones, L. H.; Badger, R. M.; Moore, G. E. *J. Chem. Phys.* **1951**, *19*, 1599.

(10) The experimental energy difference between the cis and trans forms is 0.5 kcal/mol.[9] The calculated difference is 0.9 kcal/mol.

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

(12) Although there may be resonance contributions to the acidity of acetic acid, these must be due to the effect of resonance on the initial-state charge distribution. See ref 2.

(13) Siggel, M. R. F.; Thomas, T. D., unpublished results.