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Articles

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Acidity of Nitrous and Nitric Acids

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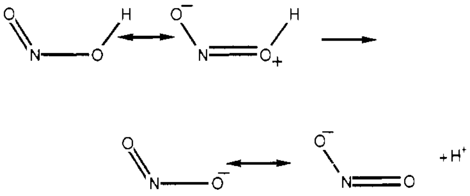
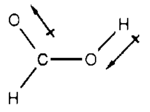
The origin of the acidity of nitrous and nitric acids was studied via an analysis of the results of ab initio calculations using the 6-311++G** basis set. The difference in energy between the *Z* and *E* conformers of nitrous acid could be reproduced when correction was made for electron correlation, and the gas-phase ionization energies of nitrous and nitric acids were satisfactorily reproduced by the calculations. With both acids, structural effects on ionization were minimal, with only a small shift in the nitrogen position. The electron population was greater at the hydroxyl oxygen than at the other oxygens in the acids, and the changes in population on ionization were small. The changes in electron populations were not in accord with the common views of resonance interactions in these compounds. It is concluded that the polarization of the charge density that is present in the acids is the main source of the acidity of these compounds.

The increased acidity of compounds such as nitrous acid as compared to water is frequently related to the increase in resonance interactions on going from the acid to the anion.[1] Thus, one would write where the equivalent structures for the anion are assumed to contribute more to stabilization than does the zwitterionic structure for the acid. Recent studies of the origin of the acidity of acetic acid[2,3] suggest that this interpretation may not be correct. In this case, it appears that the polarization of the carbonyl group in the acid is the main source of the increased acidity. Nitrous acid should provide an interesting comparison because the electronegativity difference between oxygen and nitrogen is less than that between oxygen and carbon.

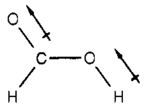


It seems appropriate to first consider the structure of nitrous acid. Whereas with formic acid, the *Z* conformer (**1Z**) is preferred over the *E* form (**1E**) by 4.0 kcal/mol,[4] the energies of the two conformers of nitrous acid have the reversed relative energy, with the *E* conformer (**2E**) having the lower energy by 0.5 ± 0.2 kcal/mol.[5] However, at the 3-21G level, **2Z** was calculated to have a lower energy than **2E**,[6a] and we have found the same to be true using the 6-31G* basis set.[6b] In the case of formic acid, it was necessary to use larger basis sets and to correct for the effect of electron correlation in order to obtain a calculated energy difference between **1Z** and **1E** that agreed with the experimental results.[7] In the present case, calculations at the 6-31G* geometries using the 6-311++G** basis set, which is effectively triple ζ and includes diffuse functions and polarization functions on all atoms, led to the correct ordering of the energies (Table I). In order to see if diffuse functions had an effect on the geometry, optimization also was done by using the 6-31++G** basis. The structural parameters changed only slightly (Table Ic). In addition, the effect of correcting for electron correlation was examined by using the 6-311++G** basis set and the Møller–Plesset perturbation theory.[8] This led to a change in relative energy by 1.0 kcal/mol favoring **2Z**, in good accord with the experimental result.



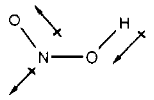
1Z

$\mu = 1.98D$



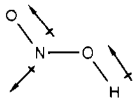
1E

$\mu = 4.60D$



2Z

$\mu = 1.55D$



2E

$\mu = 1.45D$

The calculated structural parameters for the two forms of nitrous acid are in good accord with those of the experimental structures. The bond lengths are, as usual, systematically underestimated because of neglect of both electron correlation and the anharmonicity in the stretching vibrations.[9] The decreases in N=O and OH bond lengths on going from **2Z** to **2E** and the corresponding increase in the N—O bond length are well reproduced. In addition, the decreases in both O=N—O and N—O—H bond angles on going from **2Z** to **2E** are in accord with the experimental results.[5]

Structurally, formic and nitrous acids appear rather similar. Why should the relative energies of the conformers differ in the observed fashion? In the case of formic acid, the *Z* conformer has the C–O and O–H bond dipoles aligned in an attractive orientation that is not present in the *E* conformer, and this leads to the observed conformational preference. The same interaction is present in nitrous acid. However, in the latter, there is additionally an atomic dipole at nitrogen associated with the lone pair. The interaction of the atomic dipole with the O–H bond dipole will stabilize **2E**. Apparently, the two interactions are energetically

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Table I. Energies and Structures

a. Energies

	energy, hartrees				
			6-311++G**//6-31G*		
compd	6-31G*//6-31G*	6-31++G**//6-31++G**	RHF	MP2	MP3
cis-nitrous acid (**2Z**)	−204.63994	−204.65312	−204.70678	−205.29244	−205.28117
trans-nitrous acid (**2E**)	−204.63768	−204.65249	−204.70702	−205.29379	−205.28281
nitrite ion	−204.06567		−204.14844	−204.74444	−204.72113
nitric acid	−279.44426		−279.53490	−280.33575	−280.31067
nitrate ion	−278.91297		−279.01128	−279.80913	−279.77904

b. Energy Differences

	energy, kcal/mol				
			6-311++G**//6-31G*		
compd	6-31G*//6-31G*	6-31++G*//6-31++G*	RHF	MP2	MP3
cis-nitrous acid (**2Z**)	0.0	0.0	0.0	0.0	0.0
trans-nitrous acid (**2E**)	1.42	0.39	−0.15	−0.85	−1.03
nitrite ion + H^+	360.4		350.5	344.7	352.5
nitric acid	0.0		0.0	0.0	0.0
nitrate ion + H^+	333.4		328.6	330.5	333.6

c. Structures, 6-31G* (6-31++G**)

		length, Å			value, deg	
compd	bond	calcd	obsd[5]	angle	calcd	obsd[5]
cis-nitrous acid (**2Z**)	N=O	1.161 (1.161)	1.185	O=N—O	113.74 (113.92)	113.7
	N—O	1.328 (1.327)	1.392	N—O—H	107.56 (108.38)	104.0
	O—H	0.960 (0.955)	0.982			
trans-nitrous acid (**2E**)	N=O	1.153 (1.152)	1.170	O=N—O	111.36 (111.74)	110.7
	N—O	1.346 (1.344)	1.432	N—O—H	105.38 (105.76)	102.1
	O—H	0.951 (0.947)	0.958			
nitrite ion	N—O	1.229		O—N—O	116.70	
nitric acid	N—O3	1.188	1.211	O3—N—O2	116.06	115.9
	N—O4	1.172	1.199	O4—N—O2	114.78	113.8
	N—O2	1.334	1.406	N—O2—H	105.33	102.2
	O—H	0.955	0.964			
nitrate ion	N—O	1.226				

Table II. Bond Properties, 6-311++G**//6-31G*[a]

compd	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	ϵ
cis-nitrous acid (**2Z**)	N=O	0.5003	0.6615	0.756	0.5998	−1.7028	−1.5218	0.9368	0.119
	N—O	0.5914	0.7374	0.802	0.4022	−1.0484	−1.0216	1.0170	0.026
	O—H	0.7868	0.1728	4.552	0.3733	−2.0331	−1.9837	1.2139	0.025
trans-nitrous acid (**2E**)	N=O	0.4927	0.6611	0.745	0.6103	−1.7510	−1.5420	0.9130	0.136
	N—O	0.6004	0.7459	0.805	0.3851	−0.9970	−0.9681	1.0237	0.030
	O—H	0.7807	0.1702	4.587	0.3838	−2.1242	−2.0691	1.2818	0.027
nitrite ion	N—O	0.5567	0.6726	0.828	0.5124	−1.3930	−1.3099	1.0956	0.063
nitric acid	N—O3	0.5772	0.6106	0.945	0.5663	−1.5363	−1.3469	1.3077	0.141
	N—O4	0.5650	0.6074	0.930	0.5864	−1.6041	−1.3928	1.2853	0.152
	N—O2	0.6276	0.7063	0.889	0.4096	−1.1514	−1.0124	1.1554	0.137
	O2—H	0.7907	0.1647	4.802	0.3758	−2.1538	−2.0939	1.3475	0.029
nitrate ion	N—O	0.5968	0.6292	0.949	0.5210	−1.4250	−1.2630	1.3005	0.128

[a] r_A is the distance from the first atom to the bond critical point in Å, and t_B is the distance from the second atom to that point. R is the ratio of r_A to r_B, and ρ_c is the charge density at the bond critical point in e/au^3. The λ's are the second derivatives of ρ with respect to the coordinates, and ϵ is the ellipticity ($=\lambda_1/\lambda_2 - 1$). In nitric acid, O3 is syn to the proton.

comparable, leading to a rather small difference in energy between the two forms. A corollary of this explanation is that the N=O and N–lone pair dipoles are about equal and that the dipole moment will be dominated by the hydroxy group. Thus, the dipole moments of the two rotamers should be about the same. This is found to be true experimentally (**2Z**, 1.55 D, **2E**, 1.45 D).[5]

The 6-31G* optimized geometries for nitric acid, nitrate ion and nitrite ion are available.[6] The 6-311++G** energies were calculated at the 6-31G* geometries and are listed in Table I. Here, a quantity of interest is the gas phase ionization energy. The calculated energy differences are given in Table Ib. In order to compare them with the experimental values,[10] it is necessary to correct them for the change in zero-point energy associated with the cleavage of an O–H bond, which is about 9 kcal/mol. The calculated ΔH for the ionization of nitric acid is then 325 kcal/mol (experimental value 325 ± 3 kcal/mol),[10] and that for nitrous acid is 344 kcal/mol (expt. 338 ± 4 kcal/mol). It can be seen that the calculated energies are quite satisfactory, indicating the wave functions should be suitable for further analysis.

In order to examine the changes that occur on going from the acids to their anions, we have found it useful to examine the change in electron populations that may be derived from the calculated wave functions. The Mulliken populations,[11] which are easily obtained, are not useful for our purpose because of the arbitrary fashion in which the charge distribution is partitioned between

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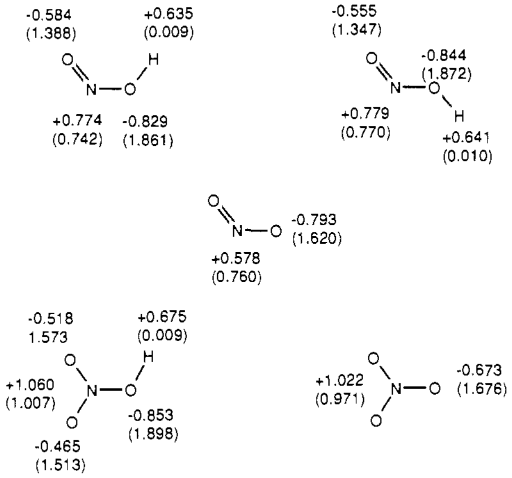

Figure 1. Atomic charges and π-electron populations (in parentheses).

atoms.[12] Therefore, we have used Bader's theory of atoms in molecules.[13]

For each pair of bonded atoms there exists a *bond path*, which is the path of maximum charge density ($\rho = \psi\psi^*$) connecting the two atoms. The point along the bond path that has the minimum charge density is known as the *bond critical point*. Although a minimum along the path, it represents a maximum in charge density in directions perpendicular to the bond path. The locations of the bond critical points are given in Table II. The points have the characteristic that they move away from the more electronegative atom. It can be seen that the ratio (R) of the distances from the atoms to the bond critical points always favors the more electronegative oxygen atom. It is interesting to note that R is smaller for the N–OH bond in nitrous acid than for that in nitric acid. This suggests that the difference in electronegativity between nitrogen and oxygen in the latter is greater than in the former, and this is reasonable in that the two nonhydroxylic oxygens attached to nitrogen in nitric acid will increase its electronegativity. The table also gives the charge density at the bond critical point, which increases with increasing double-bond character for any given pair of atoms. The λ's are the components of the Laplacian of the charge distribution (i.e. the second derivatives of the charge density with respect to the three principal directions at the bond critical points), and for a bonded pair of atoms, two are always negative and one (along the bond) is positive. The final quantity, ϵ, is the ellipticity and is defined as $\lambda_1/\lambda_2 - 1$. It is a measure of the relative "softness" of the charge distribution in directions normal to the bond path.

Pairs of atoms are separated by surfaces across which the derivative of ρ is zero, and these are known as zero-flux surfaces.[13] For a given pair of atoms, one starts at the bond critical point and finds the set of paths for which the charge density decreases most rapidly. These paths define the zero-flux surface, and the set of these surfaces serves to partition a molecule into a set of atoms. The importance of these volume elements lies in the fact that within each the usual theorems of quantum chemistry such as the virial theorem apply. The electron populations were obtained by numerical integration of the charge density within the boundaries thus described. The n_T values are the total populations for the atoms, whereas $n\pi$ gives just the π (out-of-plane) component. The kinetic energy of the electrons associated with a given atom was obtained at the same time. The virial theorem requires that the total energy of a given atom be equal to minus the kinetic energy. In order that the calculated atomic kinetic energies would correctly sum to minus the total energy, they were multiplied by $-V/T - 1$ where $-V/T$ is the virial defect found in the ab initio calculations. The results are presented in Table III. It can be seen that the atomic kinetic energies sum to a value that differs from the negative of the total energy by only a small amount.

Table III. Atom Properties, 6-311++G**/6-31G*[a]

compd	atom	n_π	n_T	T
cis-nitrous acid (**2Z**)	N	0.7420	6.2259	53.8187
	O3	1.3884	8.5836	75.2416
	O2	1.8606	8.8285	75.3186
	H	0.0094	0.3653	0.3328
	sum	4.0004	24.0033	204.7117 ($E = -204.7068$)
trans-nitrous acid (**2E**)	N	0.7702	6.2506	53.8136
	O3	1.3472	8.5449	75.2400
	O2	1.8722	8.8443	75.3154
	H	0.0104	0.3586	0.3355
	sum	4.0000	23.9984	204.7045 ($E = -204.7072$)
nitrite ion	N	0.7602	6.4129	53.8671
	O	1.6200	8.7933	75.1405
	sum	4.0002	23.9995	204.1481 ($E = -204.1484$)
nitric acid	N	1.0066	5.9396	53.7418
	O3	1.5734	8.5179	75.1046
	O4	1.5134	8.4648	75.0982
	O2	1.8978	8.7533	75.2778
	H	0.0086	0.3251	0.3124
	sum	5.9996	32.0007	279.5348 ($E = -279.5349$)
nitrate ion	N	0.9706	5.9776	53.7475
	O	1.6762	8.6726	75.0883
	sum	5.9992	31.9954	279.0124 ($E = -279.0113$)

[a] n_π is the π-electron population, n_T is the total population. Subtract 2.0 from the O and N values to obtain the valence electron populations. T is the kinetic energy corrected for the virial defect, and E is the calculated total energy. Both are in units of hartrees. In nitric acid, O3 is syn to the proton.

In order to facilitate comparisons, the populations were converted to atomic charges by subtracting the nuclear charge from each and are presented in diagrammatic form in Figure 1. In addition, the π-electron populations are given in parentheses.

The electron population at the nitrogen of nitric acid was somewhat less than that for nitrous acid, and this may readily be attributed to the presence of an additional electronegative oxygen. In both cases, nitrogen bears a positive charge, and the formal positive charge at the nitric acid nitrogen that appears in the Lewis structures does not find a counterpart in the difference in electron populations for the two acids. In all of these species, the nitrogen is electron deficient because of the greater electronegativity of the oxygens.

With both acids, the oxygen with the largest electron population was that bearing the hydroxyl hydrogen. This may appear strange in terms of the ground-state resonance structures shown above. But it is reasonable when one recognizes that the electronegative hydroxy oxygen is able to withdraw charge from both the nitrogen and the hydrogen, whereas the other may withdraw charge only from the nitrogen. On ionization, the population at the hydroxyl oxygen decreases, whereas that at the others increase. All of the changes in population are relatively small, which is reasonable in view of the small electron populations associated with the hydrogens.

One way in which to visualize the changes that occur on going from the acid to its anion is to compare the projection density functions as defined by Streitwieser.[14] Here, for a planar molecule, one sums the charge density above and below a given point in the molecular plane and assigns the total to that point. Plots of the projection density for nitrous acid and nitrite ion are given in Figure 2, and those for nitric acid and nitrate ion are given in Figure 3.

If one compares the projection plots in Figure 2, one finds that the coordinates of the oxygens of nitrous acid do not change on ionization; rather, there is a small shift in the position of the nitrogen. The same is true with nitric acid (Figure 3). The contour values also are essentially the same for each acid–anion pair, except

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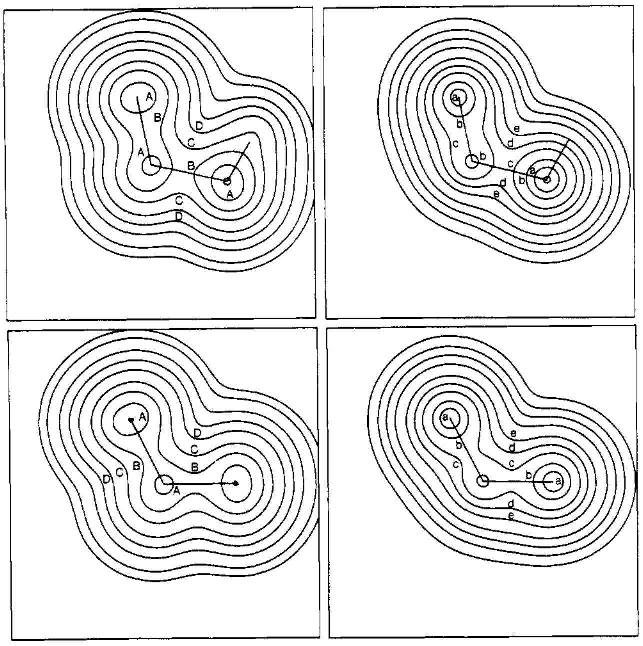

Figure 2. Projection density functions ($\int \rho \, dx$) for (Z) nitrous acid (upper left = total density, upper right = π density) and nitrite ion (lower left = total density, lower right = π density). The contour values are $A = 1.6$, $B = 0.8$, $C = 0.4$, and $D = 0.16$ e/au^2 and $a = 0.4$, $b = 0.16$, $c = 0.08$, $d = 0.04$, and $e = 0.016$ e/au^2. The projection density function for (E)-nitrous acid is essentially the same except for the placement of the hydrogen.

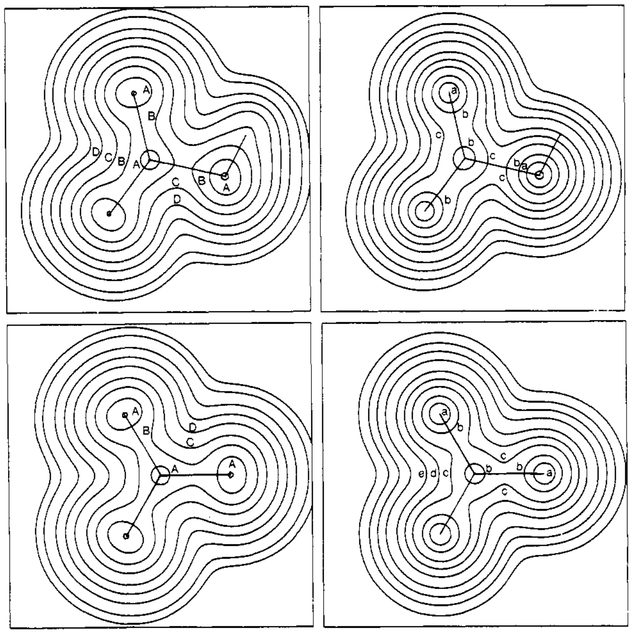

Figure 3. Projection density functions for nitric acid (upper left = total density, upper right = π density) and nitrate ion (lower left = total density, lower right = π density). The contour values are the same as for Figure 1.

near the central nitrogen. Clearly, there is a minimal change on going from the acid to the anion. The similarity between the two acids and between the two anions also may be noted. The projection density contours of nitrous acid are almost superimposable with the corresponding contours of nitric acid in the region away from the extra oxygen in the latter, and the locations of the atoms are almost superimposable. The same is true with the anions.

It is possible that the total density masks some interesting changes in the π-electron systems for these molecules. Projection density maps for the π electrons of the four compounds also are shown in Figures 2 and 3. The population analysis indicates that the π-electron populations at the hydroxy oxygens of the acids were larger than at the other oxygens, and this also is evident in the projection density plots for the π electrons. In the absence of charge polarization, one would expect that the hydroxy oxygen in nitric acid would have 2 π electrons in the lone pair, the nitrogen would have 1 π electron and that the other oxygens would have 1.5 electrons each. The calculated populations are close to these values. The π population at the hydroxy oxygen is 0.1 electron less than expected on this basis, but is not surprising in view of the large total population at this oxygen. A strong electron shift toward the oxygen in the σ system will normally be partially compensated by back-bonding in the π system. The π populations in nitrous acid fit a similar pattern. Here, in the absence of charge polarization one would expect 2 π electrons at the hydroxy oxygen and 1 electron at each of the nitrogen and the other oxygen. The calculated value at the hydroxy oxygen is again somewhat less for the same reason as indicated above.

The atom energies fit a similar pattern. If the volume assigned to a given atom is approximately constant, an increase in electron population will result in an increase in the kinetic energy and a decrease in the total energy that is twice as large according to the virial theorem. The hydroxy oxygens, with the larger electron populations, have the larger kinetic energies and the lower total energies. The hydrogen of nitric acid, which has a lower electron population than that of nitrous acid, has the lower kinetic energy and the higher total energy.

The results of these calculations are in accord with expectations based on the electronegativities of the atoms forming the bonds and again point out the importance of the charge polarization in the acids themselves. Although some π charge density shifts occur that might be ascribed to a resonance interaction, this is not the dominant factor in the charge density distribution. The latter is mainly controlled by the σ (in plane) interactions between atoms. We conclude 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.

Calculations

The calculations were carried out by using GAUSSIAN-82.[15] The charge density integrations were carried out by using PROAIMS.[16]

Acknowledgment. The MicroVax II computer used in this study was provided by a NSF instrument grant, and the CSPI array processor used in the numerical integration of the charge density was provided by a DOD instrument grant. I thank Dr. Teresa LePage for converting the PROAIMS code to run on the array processor. This investigation was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

Registry No. Nitrous acid, 7782-77-6; nitric acid, 7697-37-2.

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