Acidities of Nitrous and Nitric Acids

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The energies of nitrous and nitric acid and their anions were calculated at the MP2(FC)/6-311++G(2d,2p) level. Their acidity was related to the acidity of hydroxylamine derivatives using isodesmic reactions. This procedure reveals that the molecules of HNO_2 and HNO_3 are strongly stabilized (by 119 or 206 kJ·mol^{-1}, respectively) but their anions are stabilized even more (by 282 or 428 kJ·mol^{-1}). The acidity of these acids is thus caused by the low energy of their anions and not by the high energy of the acid molecules, similarly to the case of carboxylic acids. This stability may be partly due to resonance but the contribution of this effect can only be estimated. Correlation of the acidities of various acids with the inductive and polarization parameters led to the following estimate: in the case of nitrous acid 46 % of the acidity enhancement is due to resonance while in the case of nitric acid it is 25 %.

Introduction

The strong acidity of nitric and nitrous acids – both in the gas phase and in aqueous solution – has been attributed, within the framework of the classic theory of resonance, to resonance in their anions.[1] Description of their structure by resonance formulae is still considered as convenient[2] and used in textbooks; it is a completely analogous explanation to the case of the relatively strong acidity of carboxylic acids. An alternative theory was suggested first for carboxylic acids[3] and then extended to nitrous and nitric acids:[4,5] the origin of the acidity is seen in the charge distribution and in the electrostatic potential of the uncharged molecules of the acids. In the case of carboxylic acids, the problem raised a vivid discussion[6–11] and complete agreement has not yet been reached. In our opinion, the problem can be rationalized (and for the greater part solved) if it is divided into two independent questions:[7,10]
a) Is the acidity of the isolated molecules caused by the low energy of their anions or by the high energy of the acid molecules?
b) Is the acidity dependent on the resonance in the anions (or also in the acid molecules)?

In the case of carboxylic acids, in our opinion the first problem has been solved[10] using the framework of isodesmic reactions.[12,13] Concerning the second problem, several models were advanced estimating the contribution of resonance with a fair agreement to approximately one third of the acidity enhancement.[8–10]

In the present article, the above-mentioned approach is applied to the acidity of nitrous and nitric acid. The procedure is not always self-evident since the choice of reference compounds is not as straightforward as for carboxylic acids but, in our opinion, it is just the application of the methods of organic chemistry that may shed light on the problem from a new standpoint. The article will be divided into two sections corresponding to the two questions a) and b). The first part is much more important since the question sub a) can be answered unambiguously. The solution makes use of isodesmic reactions and of the energies calculated by ab initio MO methods.[14] In the second part, only one possible model will be mentioned for estimating the resonance contribution, which is supported by experimental gas-phase acidities. Let us stress that our approach is based either on the experimental energies (mainly the gas-phase acidities) or on the calculated energies that can be related to some experimental values; any reference to fictive or theoretical structures is avoided.

Results and Discussion

Energy of the Anions and of the Acid Molecules

The relatively strong acidity of carboxylic acids has always been evaluated with alcohols as a natural reference.[3,6–11] By the same token, a reference compound for nitrous acid is a hydroxylamine derivative. In the isodesmic and homodesmotic[15] reaction, see Equation (1), the molecule of nitrous acid is constructed from nitrosomethane and *N*,*N*-dimethylhydroxylamine. The reaction energy $\Delta_1 E$ is a measure of the interaction of the groups N=O and OH in the molecule of nitrous acid. Of course, Equation (1) represents only one possible solution but its merit is that it oper-

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Table 1. Calculated energies and some bond lengths of nitrous and nitric acid and of reference compounds.

	E a.u.	N=O [Å]	N–O [Å]
HNO_2 *sp*	–205.3335699	1.193[a]	1.397[a]
HNO_2 *ap*	–205.3345614	1.178[a]	1.433[a]
$NO_2^–$	–204.7851469		1.270
HNO_3 *sp* (planar)	–280.3949067	1.217[b], 1.205[b]	1.413[b]
$NO_3^–$ (planar)	–279.8677848		1.265[c]
$CH_3N=O$	–169.4401081	1.224	
$(CH_3)_2NOH$ *ac* [d]	–209.8640456		1.456
$(CH_3)_2NOH$ *sc*	–209.8599901		1.433
$(CH_3)_2NO^–$	–209.2526309		1.408
$(CH_3)_3N–O$	–249.0418991		1.368
$(CH_3)_3N$	–174.0148768		

[a] These figures agree with the experimental values[16] with the greatest deviation of 0.008 Å, this is a better agreement than that obtained at the level CCSD(T)/cc-PVQZ(spdf,spd)[17] and much better than at the levels B3LYP/6-311G(d,p)[18] or BH&HLYP/6-311G(d,p)[19]. [b] Agreement with the experimental values[16] within 0.007 Å. [c] Experimental value[20] 1.253(6) Å. [d] The O–H bond eclipsed with the electron lone pair on N.

ates exclusively with stable and well-characterized molecules, even when their enthalpies of formation have not been experimentally determined. Introducing the methyl groupsw into Equation (1) has another advantage, that is, molecules of similar polarizability[3,7] are compared. If in Equation (1) hydroxylamine were used instead of *N*,*N*-dimethylhydroxylamine, the results would not be significantly altered.

$$O{=}N–CH_3 + (CH_3)_2N–OH = O{=}N–OH + (CH_3)_2N–CH_3 \qquad (1)$$

Similarly, the interaction of the two oxygen atoms in the nitrite anion is measured by the reaction energy Δ_2E of the reaction of Equation (2); by this interaction the two oxygen atoms become equivalent.

$$O{=}N–CH_3 + (CH_3)_2N–O^– = O{=}N–O^– + (CH_3)_2N–CH_3 \qquad (2)$$

An isodesmic reaction generating nitric acid from its component functions would be somewhat complex. On the other hand, one can relate nitric acid to nitrous acid in a simple way by Equation (3).

$$O{=}N–OH + (CH_3)_3N–O = O{=}N(O)–OH + (CH_3)_3N \qquad (3)$$

The reaction energy Δ_3E represents the difference between the interactions in nitric and nitrous acid; the total interaction in nitric acid is given by $\Delta_1E + \Delta_3E$. Similarly the relation of nitrate and nitrite anions is represented by Equation (4); the total interaction within the nitrate anion is given by $\Delta_2E + \Delta_4E$.

$$O{=}N–O^– + (CH_3)_3N–O = O{=}N(O)–O^– + (CH_3)_3N \qquad (4)$$

Ab initio calculated energies of the compounds involved in Equations (1) to (4) are listed in Table 1. Few compounds can exist in equilibrium of two conformers, as given in the footnotes to Table 1, but the pertinent energy differences are negligible. Nevertheless, the energies of the isodesmic reactions, Δ_1E to Δ_4E, were always calculated for the equilibrium mixtures of conformers at 298 K (Table 2).

In the qualitative sense, the results are the same for nitrous and nitric acid. The molecule of HNO_2 is strongly stabilized (by more than 100 kJ·mol^{-1}) but the anion $NO_2^–$ is stabilized much more (almost by 300 kJ·mol^{-1}); the difference determines the acidity. For HNO_3 and $NO_3^–$ the values are almost two times greater (200 and 400 kJ·mol^{-1}, respectively). In relation to these figures, any arbitrariness in the isodesmic reactions and imperfections of the theoretical model are of no consequence. Even the conformations of some of the compounds involved are irrelevant from this point of view. Therefore, our results are in contrast to the claim[4,5] that the acidity is due to the initial-state charge distribution.

Correlating our results to experimental values is of vital importance to our approach. For the two conformers of HNO_2, antiperiplanar *ap* and synperiplanar *sp*, we calculated the energy difference of 2.6 kJ·mol^{-1} (the *ap* conformer is more stable); the experimental value[21] is 2.1 kJ·mol^{-1}. The low-level calculations[3] (RHF/3-21+G) gave 3.8 kJ·mol^{-1}. Recent calculations[18] produced satisfactory results only at the MP2/6-311G(3df,2p) or G2M(RCC,MP2) levels while at the QCISD(T)/6-311G(d,p) and lower levels even the order of stability was reversed. The conformational energy is evidently too small and its calculations are sensitive to the level employed. A better idea about the reliability of the calculations can be obtained from the relative acidities of HNO_3 and HNO_2, that is, from Equation (5).

$$HNO_3 + NO_2^– = NO_3^– + HNO_2 \qquad (5)$$

Our calculated reaction energy Δ_5E is –57.8 kJ·mol^{-1} (see Table 2) while the experimental Gibbs energy[9] $\Delta_5G°$ is –54.4 kJ·mol^{-1} and the enthalpy[22] $\Delta_5G°$ is –66.6 kJ·mol^{-1}.[23] Calculations at the RHF/3-21+G level yielded[4] –107 kJ·mol^{-1}. This theoretical model was obviously insufficient and further results of this paper[4] can be questioned.[23]

Table 2. Calculated acidities and energies of the isodesmic reactions (kJ·mol^{-1}).

	Formation of the acid	Formation of the anion	Acidity
HNO_2 *ap* [Equations (1) or (2)]	–116.3	–281.7	–165.4
HNO_2 *sp* [Equations (1) or (2)]	–118.9	–281.7	–162.8
HNO_2 equil. mixture	–118.2	–281.7	–163.5
HNO_3 – HNO_2 [Equations (3) or (4)]	–88.2	–146.0	–57.8
HNO_3	–206.4	–427.7	–221.3

Effect of Resonance

When we accept that the strong acidity of both HNO_2 and HNO_3 is due to the low energy of their anions, it does not follow that this low energy is a consequence of resonance. However, resonance may be defined differently and its effect cannot be calculated unambiguously. It is necessary to design a molecule, more or less fictive, without resonance but otherwise similar to the molecule under investigation. In the case of carboxylic acids, several different models were designed and it may be considered as a remarkable agreement that some of them evaluated the effect of resonance to 30–40% of the increased acidity.[8–10] Let us mention here only one model,[10] originated from the fundamental idea of Taft,[9] that relates to stable molecules and is based exclusively on the experimental data. The relative gas-phase acidities of common oxygen acids ROH are defined by Equation (6).

$$R\text{–}OH + OH^- = R\text{–}O^- + H_2O \qquad (6)$$

In the absence of resonance effects, the relative acidity $\Delta_6G°(298)$ can be empirically approximated[9] as a linear function of the inductive constants σ_I and polarizability constants σ_α. For 15 selected R substituents (H, seven alkyl groups, $CH_2C_6H_5$, CH_2OCH_3 and five fluorinated alkyls – mostly organic compounds since derivatives of hydroxylamine are not at our disposal) we obtained Equation (7).

$$\Delta_6G°(298) = 1603(4) - 299.8(73)\sigma_I + 97.9(73)\sigma_\alpha \ (\text{kJ·mol}^{-1}) \qquad (7)$$

Figure 1 is a graphical representation of this relationship, where experimental[9] $\Delta_6G°(298)$ values were plotted against the right-hand side of Equation (7). The points for HNO_2 and HNO_3 in this graph deviate by the assumed contribution of resonance, 75 or 56 kJ·mol^{-1}, respectively. It follows that resonance should be responsible for 46% or 25%, respectively, of the enhanced acidity. (In the case of HNO_3 this estimate is biased since it starts from the group NO_2 and hence does not include the resonance already involved in this group.) Taking into consideration all the approximations, it seems safe to conclude that resonance is a very important factor in the case of HNO_2 and less important in the case of HNO_3. The explanation of this difference may be found in the so-called crossed conjugation in the anion NO_3^-.

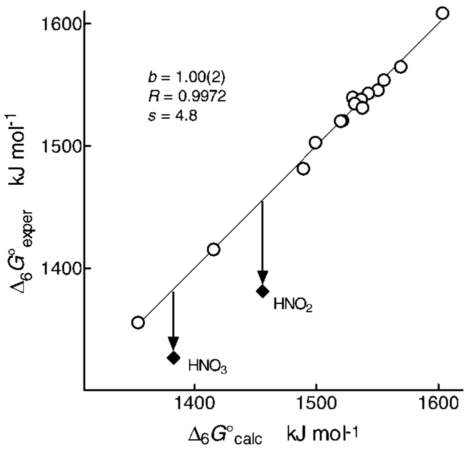

Figure 1. Plot of the experimental gas-phase acidities of the oxygen acids without resonance, Equation (6), vs. their values calculated according to the empirical Equation (7); the points for HNO_2 and HNO_3 deviate due to resonance as shown by the arrows.

In the case of carboxylic acids, a further attempt was made to evaluate separately the effect of resonance in the anion and in the acid molecule.[10] Application of this process to nitrous or nitric acid would require the construction of complex isodesmic reactions involving unstable or nonexisting molecules; their enthalpies of formation should be calculated using high-level models. We have rejected this approach as it is too sophisticated.[25]

In addition to energies, the theory of resonance predicts qualitatively changes of other observable quantities. For our compounds, the effect on the bond lengths should be the most conspicuous: N=O double bonds in HNO_2 and HNO_3 should be lengthened, N–O single bonds shortened. In the anions NO_2^- and NO_3^- the N–O bonds are equal and should be intermediate between single and double bonds. The latter prediction is fulfilled (see Table 1) but the former is not, particularly as the N=O bonds in HNO_2 are not longer than in $CH_3N{=}O$. Similar results were obtained when testing the resonance theory on amides and carboxylic acids: the single bonds were shortened but the C=O bond was lengthened insignificantly.[27] One must conclude that the resonance formulae are a fairly approximate picture. They can describe some observable quantities surprisingly well but can fail in other cases.

Conclusions

The framework of isodesmic reactions enables us to conclude that the strong acidity of HNO_2 and HNO_3 is caused by the low energy of their anions. The energy of the acid molecules is not particularly high; on the contrary it is also lowered and causes an opposite effect (acid weakening). The energies of the isodesmic reactions are so great that any defect of the model, either in the choice of reference compounds or in the computational procedure, is insignificant. On the other hand, the question of whether the acidity is due to resonance is inexact and can be answered only approximately. Resonance is operating but is less significant than the inductive effect, with HNO_3 maybe less than with HNO_2. In our opinion, this problem is not of particular importance since resonance means always a difference between a real molecule and an artificial formalism. In our opinion it has been merely a tool for identifying the difference between real structures and primitive traditional formulae.

Computational Details

Energies of nitrous and nitric acids, of their anions and of reference compounds were calculated at the levels MP2(FC)6-311++G(2d,2p)//MP2(FC)6-311++G(2d,2p) (Table 1) and B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p)[23] with the

GAUSSIAN 03 program.[14] All reasonable conformations were taken into consideration and calculations were started from the pertinent near structures. Planarity or any symmetry was never anticipated. All structures were checked by vibrational analysis and behaved as energy minima.

Population of conformers was calculated with the standard approximation that $\Delta G°(298) \approx \Delta E$; with this population the effective ΔE for the equilibrium mixture of conformers for each compound was obtained. The energies of isodesmic reactions, $\Delta_1 E$ to $\Delta_4 E$, were calculated with these effective ΔE values.

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[23] In previous work, for instance see ref. [24], we usually got a better fit with the Gibbs energies than with the enthalpies due to less dependability of the latter. In order to test the dependence of our results on the theoretical model we calculated the reaction energy $\Delta_5 E$ still at the level B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) and obtained $-65.4\ \mathrm{kJ{\cdot}mol^{-1}}$. This theoretical model seems to be somewhat better but note that even the inaccuracy of $10\ \mathrm{kJ{\cdot}mol^{-1}}$ would not change our final results.

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[25] Another approach could be taken by considering the valence bond theory. In the case of carboxylic acids, a reasonable estimate of resonance was obtained, ref. [26], but several possible localized structures were designed with some arbitrariness, even for structures without resonance (ethanol); moreover, the agreement with experimental acidities was very bad. Nevertheless, we agree with a referee that this would be the most important alternative to our approach.

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