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Energetic Measure for the Ionic Character of Bonds

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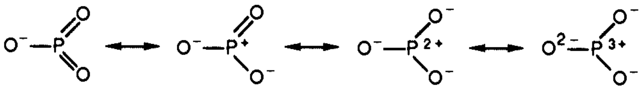
Abstract: It is proposed to measure the ionicity of bonds by the energy increase obtained on the SCF level of theory by enforcing an ionic molecular electronic structure. Exploratory calculations to diatomics show this definition to be in line with chemical experience. Applications to Y-conjugated systems such as BF_3, $AlCl_3$, NO_3^-, PO_3^-, $P(CH_2)_3^-$, and SO_3 show appreciable occupation of the valence pπ AO of the central atom in PX_3^- and SO_3, although smaller than in the nitrate ion.

I. Introduction

Population analyses[1-5] are designed to characterize molecular electronic structures by a small set of numbers like atomic charges and bond indices related to ionic character and bond strength, respectively. Such an interpretational scheme would bridge the gap between abstract quantum mechanics and intuitive ideas common throughout chemistry. However, the framework of quantum mechanics does not provide a way for a (unique) definition of the charge of an atom or the strength of a particular bond in a molecule since these quantities are not measurable. This implies that any kind of population analysis is arbitrary to some extent at least.

Although the just described point of view has never been seriously questioned, there appears to be a recent tendency to disregard the ambiguity of any population analysis and to accept atomic charges as a basis for conclusions of importance. Let us just mention an example which has partly motivated the present study. Streitwieser et al.[6] have published an interesting treatment of metaphosphate, PO_3^-. These authors considered the resonance structures **1a**-**1c**. From atomic charges q(P) for phosphorus obtained on the basis of natural AO (NAO),[3] $q(P)_{NAO} = +2.7$, or by means of the integral spatial electron population (ISEP)[5] $q(P)_{ISEP} = +3.68$, it was concluded that metaphosphate is essentially described by the valence structure **1c**. We note, however, the charges on P reported would rather support resonance structure **1d**.



1a **1b** **1c** **1d**

The implication is that the 3pπ AO on P is rather weakly occupied (NAO population of 3pπ(P) = 0.56 for PO_3^-) and that metaphosphate bears only little similarity to a Y conjugated system such as the valence isoelectronic nitrate ion. Similar but less pronounced conclusions were drawn for $P(CH_2)_3^-$ where $q(P) = 1.70$ (NAO result) was reported.[6]

It is the purpose of this article to propose and test an energetic measure for the degree of ionicity of a compound or a bond, which is at least useful to establish whether or not the limiting case of complete ionicity is approached. Our idea is simple. We compute—on the SCF level of theory—the energy increase effected by enforcing an ionic molecular electronic structure. For this purpose we first get the conventional SCF energy, E_{SCF}, of the molecule under consideration. An ionic structure is then enforced by a constraint calculation in which the cation AO's, which are unoccupied in an ionic electronic structure by definition, are deleted from the basis set. The corresponding energy is denoted $E^K{}_{SCF}$, where K labels the (cation) valence AO (one or several, see below) deleted from the basis set.

It is then proposed to consider

$$\delta E^K = E^K{}_{SCF} - E_{SCF} \qquad (1)$$

as a measure for the occupation of the K'th AO on atom A which is deleted in the ionic calculation. This approach is meaningful only within an LCAO treatment and is consequently not free of ambiguity. If one would choose very large basis sets for the remaining atoms, then δE^K could clearly be made arbitrarily small. The results presented below demonstrate that this is no serious drawback.

Table I. Basis Sets Used

atom	basis set type	origin ref	contraction scheme[a]
H	6s1p		(3111, 1)
Li	7s1p	[9]	51 (1, 1)
B···F	9s5p1d	[9]	511111 (311, 1)
Na	11s7p	[9]	52111 (1), 411 (1)
Al···Cl	11s7p1d	[9]	521111, 4111, 1[b]
			521111, 7 (111, 1)[c]
K	14s10p	[10]	6111111 (11), 51111 (1)
in $LiXH_n$:			
H	5s		311
X (C, N, O)	9s5p1d	[9]	51111, 311, 1
in AX_3:			
H	4s1p		31, 1

[a] Cation basis functions to be deleted are closed in parentheses. [b] If this atom is anionic. [c] If this atom is cationic (3p-basis functions into 2p-AO contracted, i.e., generalized contraction).

II. Technical Details of Computations

All calculations have been performed on the SCF level of theory. We started from basis sets of DZP or TZP quality used in the normal calculations. This basis is flexible enough to produce quite reliable (SCF) charge distributions. It is also not too flexible; i.e. combinations of basis functions on one atom cannot mimic an AO deleted on another atom in the modified calculation.

The primitive GTO basis sets were taken from Huzinaga's tables and contracted as listed in Table I. The polarization functions, as listed in Table II, have been optimized simultaneously at the SCF level for all molecules treated. All molecules (except $LiXH_n$ and the Y conjugated systems, see Table IV, below) were treated at the experimental geometries also given in Table II.

The modification of basis sets, i.e., the suppression of basis functions to enforce an ionic electronic structure, can be done in two different ways.

(i) In fortunate cases it is obvious that some basis functions just contribute to certain AOs. In alkaline atoms there is a clear separation between valence and core basis functions, and one can simply delete the basis functions of valence type. The effect of the valence basis function on the description of core orbitals can be easily checked by SCF calcu-

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Table II Experimental Geometries and Optimized Exponents of Polarization Functions[a]

molecule MX	r(M–X) au (ref 8)	exponents of polarizatn functns M	X
LiH	3.0155	p 0.443	p 0.157
NaH	3.5667	p 0.036	p 0.192
KH	4.2378	p 0.027	p 0.190
BH	2.3289	d 0.690	p 0.466
AlH	3.1140	d 0.484	p 0.241
HF	1.7326	p 0.873	d 1.218
LiF	2.9553	p 0.102	d 0.398
NaF	3.6396	p 0.057	d 0.384
KF	4.1035	p 0.045	d 0.315
BF	2.3860	d 0.738	d 0.878
AlF	3.1264	d 0.517	d 0.544
ClF	3.0771	d 0.835	d 0.641
HCl	2.4086	p 0.550	d 0.968
LiCl	3.8186	p 0.076	d 0.249
NaCl	4.4613	p 0.046	d 0.247
KCl	5.0393	p 0.037	d 0.221
BCl	3.2426	d 0.456	d 0.631
AlCl	4.0254	d 0.377	d 0.344
NaLi	5.31	p 0.061	p 0.153
H_2	1.4012	p 0.957	
Li_2	5.0511	p 0.129	
Na_2	5.8183	p 0.075	
K_2	7.3797	p 0.046	
F_2	2.6682	d 0.970	
Cl_2	3.7567	d 0.545	

Optimized Geometries and Exponents of Polarization Functions[a]

molecule	symmetry	geometry (distances in bohr) (angles in deg)		exponents of polarizatn functns	
$LiCH_3$	C_{3v}	r(Li–C)	3.739	Li(p)	0.455
		r(C–H)	2.066	C(d)	0.730
		<(H–C–H)	105.4		
$LiNH_2$	C_{2v}	r(Li–N)	3.268	Li(p)	0.431
		r(N–H)	1.896	N(d)	0.861
		<(H–N–H)	104.3		
LiOH	$C_{\infty v}$	r(Li–O)	3.033	Li(p)	0.088
		r(O–H)	1.768	O(d)	1.054
BF_3	D_{3h}	r(B–F)	2.445	B(d)	0.711
				F(d)	0.880
$AlCl_3$	D_{3h}	r(Al–Cl)	3.925	Al(d)	0.387
				Cl(d)	0.378
NO_3^-	D_{3h}	r(N–O)	2.317	N(d)	0.852
				O(d)	1.009
PO_3^-	D_{3h}	r(P–O)	2.768	P(d)	0.674
				O(d)	0.613
$P(CH_2)_3^-$	D_3	r(P–C)	3.153	P(d)	0.586
		r(C–H)	2.029	C(d)	0.345
		<(H–C–H)	119.4	H(p)	0.770
		<(C–P–C–H)	17.3[b]		
SO_3	D_{3h}	r(S–O)	2.647	S(d)	0.763
				O(d)	0.719
B_2F_6	D_{2h}	$r(B–F_b)$	2.880	as in BF_3	
		$r(B–F_t)$	2.452		
		$<(F_t–B–F_t)$	122.0		
		$<(F_b–B–F_b)$	86.0		
Al_2Cl_6	D_{2h}	$r(Al–Cl_b)$	4.372	as in $AlCl_3$	
		$r(Al–Cl_t)$	3.977		
		$<(Cl_t–Al–Cl_t)$	89.4		
		$<(Cl_b–Al–Cl_b)$	90.6		

[a] Optimized on the SCF level. [b] Torsion angle.

lation (with and without valence basis) for the corresponding cation. In Na^+, to give an example, deletion of the 11th s function in the 11s7p basis leads to an energy increase of 5 μh only.

(ii) A more rigorous way is to contract the basis functions in question to atomic SCF orbitals and to keep only those to be included in the calculation. To give simple examples: in Na one would contract the s basis to atomic 1s and 2s SCF-AOs if the 3s AO is to be deleted. In a PO_3^- calculation (molecular symmetry D_{3h}, z-axis perpendicular to molecular plane) one can contract the p_z basis of P to the $2p_z$ AO to make sure that no $3p_z$ contribution is present in the MOs of the metaphosphate ion. This approach is necessary if basis functions cannot be uniquely assigned to the valence space only and had to be chosen for the atoms Al to Cl.

The first approach is very easy to apply. The second one can be carried through efficiently only with the aid of integral programs allowing for generalized contraction schemes which in addition distinguish between p_x, p_y, p_z, and d_{xy}, d_{xz}, etc. orbitals.

III. Results

In Table III we have collected the results obtained for a series of mainly diatomics (formed of monovalent atoms), which cover the full spectrum between strongly ionic, e.g., KF, and covalent molecules. Besides the total energy we list the following energy increments. (a) δE^{π} is obtained by deleting just the π components of the "cation" polarization functions. The corresponding energy increment is considered as a measure of the degree of back bonding, e.g., the "back transfer" from fluorine $2p\pi$ into lithium $2p\pi$ orbitals in LiF. (b) δE^{pol} is obtained by deleting the entire cation polarization set. (c) δE^{val} is obtained by deleting the cation valence basis functions in addition to (b). In the case of cationic hydrogen this means a bare nucleus without any hydrogen basis functions.

The gross features emerging from computed energy increments given in Table III are in full agreement with chemical intuition, although there are some unexpected finer details which will be considered further below. One can clearly discern between dominantly ionic compounds, from KF to LiOH, where enforcing an ionic electronic structure (deletion of valence basis functions at the cation) leads to an energy raise by about 5 mH to about 14 mh only. The lithium compounds LiMe, $LiNH_2$, and LiOH are found in this range.

The compounds of Al with H, F, or Cl form the next group with δE^{val} ranging from about 35 mh to almost 70 mh. This indicates increased covalent contributions to bonding as compared to the (dominantly) ionic group, as expected.

The remaining compounds listed show $\delta E^{val} > 140$ mh and include the homonuclear diatomics (H_2, F_2, Cl_2), the relatively covalent BH and ClF, and the somewhat special cases BF, BCl (π backbonding), and the acids HF and HCl. A special group is formed by the alkalidimers (Li_2, Na_2, LiNa, K_2), which are distinguished by very weak covalent bonds.

The energy increments presented in Table III are expected to depend on a number of properties such as ionization potential of cationic and electron affinity of anionic atoms, bond distance (Coulomb interaction), polarizability (especially of the "anion"), and covalent contribution to bonding and backbonding. We are not aware of any interpretational scheme to analyze the energy increments in a thorough way and will not attempt to do so—but a few comments are in order.

Consider first the ionic compounds KF to LiOH in Table III. If a contribution of cation $p\pi$ AOs is allowed by symmetry (i.e., with the exception of alkali hydrides), then δE^{π} is the largest contribution which typically amounts to about 60% of the energy increment due to cationic valence orbitals (δE^{val}). This can be expressed in saying that backbonding is the energetically most important effect of cation valence orbitals. A noticeable exception is LiMe, where lithium $p\pi$ orbitals make a very small contribution (0.4 mh), which no doubt is due to the fact that the occupied e type MOs of the Me moiety (which interact with lithium $p\pi$) point away from lithium. This effect is less pronounced for $LiNH_2$ and even less for LiOH. The order of δE^{val} for LiMe (11.2 mh), $LiNH_2$ (11.3 mh), and LiOH (13.5 mh) is in fact solely due to backbonding effects. If only the energy increase due to the deletion of the lithium 2s AO is considered (3.7 mh, 1.2 mh, 0.6 mh for LiMe, $LiNH_2$, LiOH), one gets in fact a reverse ordering, which is in accord with the expected trend in ionicity.

Across the series of alkali halides we find the following expected trends: KX more ionic than NaX and this more ionic than LiX, and similarly the fluorides more ionic than the chlorides (as measured by δE^{val}).

The situation is different for the alkali hydrides LiH, NaH, and KH, which according to δE^{val} show decreasing degree of ionicity, although the effect is small since δE^{val} varies from 6.7

Table III. Energetic Effects Due to Deletion of Cationic Basis Functions

molecule "AX"	E_{SCF} basis,[a] Hartree	δE^{π} basis,[b] mHartree	δE^{pol} basis,[c] mHartree	δE^{val} basis,[d] mHartree
KF	−698.630 59	3.2	3.8	5.5
LiH	−7.983 94		5.5	6.7
NaH	−162.378 74		0.5	6.7
KH	−599.664 96		0.7	7.2
NaF	−261.342 73	5.0	5.7	7.8
KCl	−1058.666 00	4.8	5.1	8.6
$LiCH_3$	−47.024 10	0.4	7.5	11.2
$LiNH_2$	−63.053 78	7.0	10.1	11.3
NaCl	−631.372 87	6.6	7.1	11.7
LiF	−106.964 13	9.3	11.0	11.9
LiOH	−82.924 31	11.4	12.9	13.5
LiCl	−466.976 62	10.4	11.2	13.6
AlH	−242.437 36		3.1	34.9
AlCl	−701.420 91	20.1	9.4	66.5
AlF	−341.440 02	16.7	9.9	67.7
HF	−100.049 44	5.6	7.9	139.9
BH	−25.127 81		2.1	158.2
ClF	−558.833 54		18.6	189.3
BF	−124.145 71	52.1	12.4	206.0
BCl	−484.089 14	45.9	14.9	221.1
HCl	−460.042 64	4.1	12.1	225.6
K_2	−1198.275 89		0.8	23.7
Na_2	−323.689 48		0.6	36.7
NaLi	−169.276 42			46.3
Li_2	−14.865 18		2.3	47.4
H_2	−1.132 95		0.7	186.1
Cl_2	−918.874 45		22.0	293.0
F_2	−198.736 97		9.2	421.7

[a] Basis set as explained in text and Table I. [b] Basis *a* but cation π-functions deleted. [c] Basis *a* without polarization functions at A. [d] Basis *a* without polarization and valence basis functions at A.

to 7.2 mh. The only rationalization we can offer for this unexpected trend is that the smaller cores can more easily penetrate the H^- electron distribution. The larger cores of Na and especially K are more difficult to accommodate and cation valence AOs are slightly more important to compensate for the cation-core interaction with the charge cloud of H^-.

The most noticeable effect of the boron compounds BF and BCl is the relatively large backbonding: deletion of boron 2pπ AOs leads to an energy increase by 52.1 (BF) and 45.9 mh (BCl), respectively. This effect is well-known and has been discussed in the literature.[2a,c] Backbonding is less pronounced for AlF (16.7 mh) and AlCl (20.1 mh), as expected (due to the size and orbital energy of the 3p AO of Al, $\epsilon = -0.21$ h, conditions for backbonding are less favorable than for B, $\epsilon_{2p} = -0.31$ h), but is still appreciable.

Relatively large δE^{val} are found for HF and HCl, 139.9 and 225.6 mh, respectively. The ordering of δE^{val} is in agreement with intuition since it indicates HF to be more ionic than HCl. Since δE^{val} for HF and HCl is the energy increase on deleting all basis functions on H, its magnitude is not so unexpected. The "bare" proton penetrates the electron distribution of "F^-" and "Cl^-" to an appreciable extent and leads to appreciable distortions (cusp conditions) which cannot be properly described in the absence of hydrogen basis functions.

For the remaining covalent (or dominantly so) compounds H_2, F_2, Cl_2, ClF, Li_2, Na_2, K_2, and LiNa we find greatly varying increases of the energy if an ionic electronic structure is enforced. The increase of δE^{val} is in any case on the order of the corresponding binding energy or even much larger, as for Cl_2, ClF, and F_2. Since F and Cl have large ionization potentials, the size of δE^{val} is quite clearly dominated by the energy required to remove an electron from the corresponding atom.

The above discussion demonstrates again that chemical bonding is influenced in an intricate way by many effects. The main result is, however, that compounds normally considered as strongly ionic show an increase in energy on deleting the cation valence AOs (δE^{val}) of about 10 mh and certainly less than 20 mh.

In Table IV we have collected the results for the series of valence isoelectronic systems BF_3, $AlCl_3$, NO_3^-, PO_3^-, $P(CH_2)_3^-$, and SO_3.

Table IV. Y-Conjugated Systems BF_3, $AlCl_3$, NO_3^-, PO_3^-, $P(CH_2)_3^-$, SO_3: Energetic Effects Due to Deletion of Central Atom Valence π-AO's

AX_3	E_{SCF}, Hartree basis[a]	$\delta E^{\pi,pol}$, mHartree basis[b]	$\delta E^{\pi,val}$, mHartree basis[c]	δE^{dimer}, mHartree	
				d	*e*
BH_3	−26.393 41	0.0	0.0	−15.0	−15.0 [f]
$AlCl_3$	−1620.501 46	9.6	31.3	−17.4	−48.7
BF_3	−323.300 78	11.0	53.7	+18.5	−35.2
PO_3^-	−565.479 23	56.5	157.0		
$P(CH_2)_3^-$	−457.708 01	32.6	154.0		
SO_3	−622.040 47	73.7	283.0		
NO_3^-	−278.994 09	23.8	321.0		

[a] Basis set as described in text and table I. [b] Basis *a* without dπ-polarization functions at A. [c] Basis *a* without π-polarization and π-valence basis functions at A. [d] Reaction energy for dimerization $AX_3 \rightarrow {}^1/_2A_2X_6$ on SCF level. [e] As *d*, but with respect to monomer with backbonding suppressed, see text. [f] Reference 7b.

Except $P(CH_2)_3^-$ (D_3 equilibrium geometry with CH_2 groups twisted by about 17° out of the CPCC plane) all these systems are considered in D_{3h} molecular symmetry. Since we are interested in Y-conjugation we have to consider the HOMOs of type a_2 and e. The central atom pπ and dπ AOs contribute to a_2 and e, respectively. $\delta E^{d\pi}$ denotes the energy increase on removal of (central atom) dπ functions, and δE^{π} on removal of dπ and the 3pπ AO. $\delta E^{d\pi}$ is an energetic measure of p$\pi \rightarrow$ dπ backbonding (from ligand to central atom), and δE^{π} is a measure of Y conjugation.

Trends of the δE^{π} given in Table IV are as expected, from electronegativities of the central atoms and ligands (by the authors at least): δE^{π} increases in the order $AlCl_3 < BF_3 < P(CH_2)_3^- < PO_3^- < SO_3 < NO_3^-$. δE^{π} for NO_3^- (321 mh), as a typical Y conjugated system, is very appreciable. The corresponding values for PO_3^- and $P(CH_2)_3^-$ are just 50% of the value found for NO_3^-. On the one hand, this implies PO_3^- and $P(CH_2)_3^-$ not to be typical Y conjugated systems; on the other hand, δE^{π} is still around 150 mh, i.e., in the order of a typical bond energy.

By virtue of the results just presented it is certainly not justified to consider PO_3^- or $P(CH_2)_3^-$ as "ionic" in the sense of the valence structures **1c** and **1d** given in the introduction, since the latter would imply that central atom valence π AOs play only an insignificant role.

Let us finally have a look at pπ–dπ backbonding as measured by $\delta E^{d\pi}$ in Table IV. We find the following increase of backbonding: $AlCl_3 < BF_3 < NO_3^- < P(CH_2)_3^- < PO_3^- < SO_3$. The trend is not unexpected: $\delta E^{d\pi}$ is rather small for the more ionic compounds $AlCl_3$ and BF_3 and is more pronounced for P and S than for N as central atoms. Somewhat remarkable is the pronounced difference between $P(CH_2)_3^-$ and PO_3^- ($\delta E^{d\pi}$ of 32.6 and 56.5 mh, respectively). We can only offer the following rationalization: σ bonds are more polar in PO_3^-, and this depletes P of electrons which lowers 3d AOs on P in energy (relative to the carbene) and leads to a more pronounced 3dπ(P) contribution to the e MOs. In a recent paper, brought to our attention through one of the referees,[11] Rajca and Lee also considered stabilities of Y-conjugated systems. These authors report total Bader populations for PO_3^-, $q(P) = +4.1$, and SO_3, $q(S) = +4.3$, besides NAO results, $q(P) = +2.70$, $q(S) = +2.78$, and conclude that "multiple bonds between first- and second-row elements have an electrostatic nature; π-overlap is unimportant". This picture appears oversimplified in our opinion. For SO_3 we obtain, see Table IV, $\delta E^{\pi} = 283$ mh and $\delta E^{d\pi} = 73.7$ mh. This strongly

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indicates that 3pπ occupation and pπ–dπ backbonding play an important role for the stability of SO_3, which is in fact the only well-known molecule out of those considered by Rajca and Lee.

The present results further allow for a rationalization of the stability of BH_3, BF_3, and $AlCl_3$ with respect to their dimers. There is clearly no backbonding in BH_3, and dimerization to B_2H_6 is favored energetically (per BH_3) by 15 mh on the SCF level ($\approx$32 mh if correlation effects are included).[7] For a discussion of BF_3 and $AlCl_3$ let us start from an electronic structure where π backbonding is suppressed and consider dimerization and backbonding as competing mechanisms of stabilization. Dimerization leads to energy lowerings of 15 mh per BH_3 unit in B_2H_6 (abbreviated $^1/_2B_2H_6$), 35.2 mh ($^1/_2B_2F_6$), and 48.7 mh ($^1/_2Al_2Cl_6$), as listed in Table IV. The trend displayed is in accordance with increasing ionic character of bonding. Backbonding stabilizes BF_3 by 53.7 mh and $AlCl_3$ by 31.3 mh, as noted for δE^π found in Table IV. This shows that π backbonding dominates for BF_3 which forms no dimer in fact.

IV. Summary

We have proposed to measure the ionic character of a bond by the energy increase, δE^{val}, obtained in SCF calculations on deletion of unoccupied cation AOs. Applications to a series of diatomics showed the corresponding δE^{val} to cluster around 10 mh for typical ionic bonds such as in LiH to NaCl. Another group of values of δE^{val}, 35–68 mH, was found for hydrides, fluorides, and chlorides of Al. The remaining diatomics considered (HF, HCl, BH, ClF, BF, BCl, H_2, F_2, Cl_2) lead to markedly larger δE^{val} which exceed 140 mH. Only the weakly bound alkali dimers (Li_2, Na_2, K_2, NaLi) are special with relatively small δE^{val} around 35 mh.

Applications to systems where Y-conjugation is possible showed a large effect for NO_3^- (δE^π = 321 mh) and a relatively small one for BF_3, which is, however, sufficiently large to rationalize the stability of the monomer with respect to dimerization. PO_3^- and $P(CH_2)_3^-$ lead to $\delta E^\pi \approx$ 155 mh. This indicates that Y-conjugation not only provides modest stabilization but also shows that a purely ionic description of the π bond, e.g., Lewis-type structure **1c** $P^{2+}(O^-)_3$ (see Introduction), is inappropriate. Our results are in line with computed 3pπ(P) populations of 0.8, 0.56 (Mulliken, NAO) for PO_3^- and 0.89 (NAO) for $P(CH_2)_3^-$ as reported by Streitwieser et al.[6] Since σ bonds, e.g., in PO_3^-, are certainly polarized, their contribution to the positive charge on P also has to be taken into consideration. If one wants to characterize this state of affairs by resonance structures, then a mixture of **1b**, **1c**, and, to a lesser extent, **1d** appears most appropriate in our opinion.

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Chemistry of Hydrotrioxides. A Comparative ab Initio Study of the Equilibrium Structures of Monomeric and Dimeric Hydrotrioxides (CH_3OOOH, $H_3SiOOOH$) and Hydroperoxides (CH_3OOH, H_3SiOOH). Relative Bond Strengths in and the Gas-Phase Acidities of Hydrotrioxides and Hydroperoxides

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Abstract: Ab initio calculations have been carried out to predict the equilibrium structures of monomeric and dimeric CH_3OOOH, $H_3SiOOOH$, CH_3OOH, and H_3SiOOH. The calculated relatively strong binding energies for the intermolecularly hydrogen-bonded cyclic dimers of the hydrotrioxides and hydroperoxides investigated (BE = 6–8 kcal/mol) support the belief that self-association is the characteristic structural feature of these species. Ab initio calculations of the theoretical acidities, defined as the energy differences between the energy minima for the neutral molecules and those for the corresponding anions, reveal the following order of the gas-phase acidities: $H_3SiOOOH > CH_3OOOH > H_3SiOOH > CH_3OOH$. The investigation of relative bond strengths indicates that the RO–OOH bonds in the hydrotrioxides are weaker than the ROO–OH bonds, supporting the predictions from the previous thermochemical and kinetic studies that the split into RO$^\bullet$ and $^\bullet$OOH radicals is the lowest energy radical decomposition pathway available for these polyoxides.

Alkyl hydroperoxides (ROOH) and alkyl hydrotrioxides (ROOOH) are key species in oxidation of organic compounds with oxygen and ozone.[1,2] Knowledge of their structure is thus essential for studying autoxidation, in the chemistry of combustion and flames, in atmospheric chemistry, and in biochemical oxidations. Yet relatively few data on the structure of these important compounds have been published. It has already been reported that self-association is one of the most characteristic physical properties of hydroperoxides.[3] It was suggested that, at least at moderate concentrations, cyclic dimeric and, to a lesser extent, trimeric entities predominate in solutions of inert solvents.[3,4] It has also been proposed that the rate of decomposition of hydrogen-bonded hydroperoxides to give radicals is faster than homolysis of the uncomplexed hydroperoxide.[5] However, until now there has been no direct spectroscopic evidence for the various possible self-associated species.

Even less is known about the structure of recently discovered hydrotrioxides (ROOOH).[6] In order to test the hypothesis of

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