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Dissociation of Ozonide in Water

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The free energy of bond dissociation for ozonide ion radical is found to be lowered in aqueous solution by about 20 kcal/mol relative to that in the gas phase, based on electronic structure calculations. Explicit treatment of anion−water clusters indicates that the stronger hydrogen bonds to first-shell water molecules formed by O^- relative to O_3^- account for much of the lowering. Reaction field methods show that nonspecific electrostatic polarization of the bulk solvent further contributes noticeably to the lowering. The study clearly demonstrates that the aqueous free energy of ozonide bond dissociation is small, and probably endothermic. Our best semitheoretical prediction of the actual value is 5 ± 5 kcal/mol.

Introduction

Ozonide ion radical is an important component[1] in irradiated alkaline oxygenated aqueous solutions. While O_3^- itself seems to be chemically quite stable in water, it is believed[1] to be responsible for initiating many reactions through production of reactive O^- ions by means of the dissociation equilibrium $O_3^- \rightleftharpoons O_2 + O^-$, although there does not seem to be any information on the value of the equilibrium constant. Dissociation of ozonide is also significant in the gas phase, where it plays a role[2] in the D-region of the ionosphere. It is interesting in these contexts that it has been argued from indirect spectroscopic evidence[3] that the bond dissociation energy (BDE) for $O_3^- \rightarrow O_2 + O^-$ is much lower in water than in gas or in other nonaqueous condensed phases. Strong interaction of O_3^- with water has also been invoked[4] for interpretation of the results of femtosecond pump−probe experiments on the aqueous cage escape yield and recombination dynamics. Binding energies[5] and photodestruction cross sections[6] have been reported for some small clusters of O_3^- with water molecules. Larger O_3^- hydrate clusters have also been observed,[7] but no thermochemical data were reported.

Resonance Raman measurements[8] have been reported on the harmonic and anharmonic vibrational frequencies of the symmetric stretch fundamental of O_3^- complexed with Cs^+ counterion and trapped in an Ar matrix. After extrapolation to the dissociation limit using a simple model based on a Morse potential, a spectroscopic value was obtained[8] for the ozonide atomization energy in this condensed phase that was only ∼2 kcal/mol lower than in the gas phase, the latter being estimated from the best available data on heats of formation and electron affinities. Under the reasonable assumption that dissociation of neutral nonpolar O_2 is similar in gas and condensed phases, this implies that the BDE of ozonide complexed with Cs^+ in an Ar matrix is only slightly lower than in the gas phase. Similar values of the fundamental frequency but slightly smaller values of the anharmonicity have also been found[9−11] in resonance Raman studies on O_3^- at several distinct trapping sites in irradiated $KClO_3$ and $NaClO_3$ crystals. The same qualitative conclusion can be therefore be drawn in those instances,[9−11] that the BDE of ozonide in whatever form it exists in irradiated chlorate crystals is close to the BDE of isolated ozonide in gas.

A gas phase photodissociation study[12] reported the threshold for O_2^- production, which taken together with the known electron affinities of O atom and of O_2 led to a value of ≤32.0 ± 0.3 kcal/mol for the gas phase BDE of O_3^-. However, directly assembling gas phase enthalpies of formation as reported in experiments selected for inclusion in the NIST Chemistry WebBook compilation[13] consistently leads to values of ∼40 kcal/mol (as discussed in more detail later in this work), which suggests some problem in interpretation of the photodissociation study.[12]

Resonance Raman observation of the symmetric stretch mode for O_3^- in aqueous solution[3] revealed a fundamental shifted to higher frequency than in the gas phase[12,14,15] or in nonaqueous condensed phases[8−11] and to an anharmonicity about twice as large as found in the nonaqueous condensed phases.[8−11] Analysis of the harmonic and anharmonic contributions and extrapolation via a Morse potential led[3] to a value for the aqueous atomization energy much lower than was found in a crystalline environment.[8] Indeed, if it is assumed that dissociation of O_2 is similar in gas and condensed phases, then literal acceptance of the reported aqueous atomization value[3] would indicate an exothermic BDE of −29 ± 18 kcal/mol. However, the simple analysis was rather meant only to establish the qualitative conclusion that there is a considerable lowering of the ozonide BDE in the aqueous environment.

For interpretation of these various experimental findings, it would clearly be useful to have a better microscopic understanding of the effect of water on the ozonide BDE. The present work makes a contribution toward this goal through the use of electronic structure calculations. The study is particularly designed to shed light on two elementary qualitative reasons that could explain a lowering of the O_3^- BDE in water. One reason, pointed out previously,[3] can be understood with the simple Born[16] model. Thus in comparison to O_3^-, the product O^- ion occupies a much smaller cavity and consequently has a much stronger electrostatic reaction field interaction with the bulk dielectric. Another reason is that the negative charge is distributed roughly half on each of the terminal oxygen atoms in O_3^-, whereas the full negative charge is concentrated on a single center in O^-. Therefore, O^- can be expected to form stronger hydrogen bonds than O_3^- to some or all of the water molecules in the first solvation shell. The relative importance of these two mechanisms is assessed here by considering small clusters with explicit water molecules to obtain specific first

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solvation shell effects and by using reaction field theory to obtain nonspecific bulk water dielectric effects.

Computational Methods

Energies of small clusters were calculated with the Gaussian-94 program.[17] The B3LYP density functional method, which combines Becke's exchange functional[18] with the Lee−Yang−Parr correlation functional[19] was used in conjunction with the 6-31+G* basis set, which consists of a split valence[20] representation of all atoms plus polarization[21] and diffuse[22] functions on all oxygens. Analytic first derivatives were used for geometry optimizations, and at each identified stationary point analytic second derivatives were determined to verify that the point was a local minimum and to determine harmonic vibrational frequencies. Basis set superposition errors (BSSE) in cluster binding energies were corrected using the well-accepted full counterpoise method[23,24] together with separate calculations with local basis sets to allow each fragment to relax to its noninteracting equilibrium geometry. Standard statistical mechanical models[25] based on an ideal gas for translations, a rigid rotor for rotations, and a harmonic oscillator for vibrations were used to evaluate thermodynamic contributions to the electronic energies to obtain enthalpies and Gibbs free energies for each of the isolated clusters in a standard state of 1 atm and 298 K.

Additional bulk dielectric contributions to the free energies were obtained with the GAMESS program[26] as locally modified to include reaction field effects.[27,28] This stage of the study used unrestricted Hartree−Fock (UHF) wave functions with the 6-31+G* basis set. The cavity shape was adapted to the detailed shape of the solute by characterizing it as a solute electronic isodensity contour.[29] Surface polarization effects were determined with a single center grid of 974 Lebedev points on the cavity surface. In most cases the center of mass proved a satisfactory origin, but in some instances of highly nonspherical cavities it was necessary to manually search for an appropriate origin. Volume polarization effects,[27−31] which typically provide an additional reaction field stabilization of ∼10 kcal/mol for anions,[28] were also included using layers spaced by $0.1a_0$ to a thickness of $6a_0$ outside the cavity. Such large numbers of points and layers were used to strive for high precision in the calculated reaction field energies. This precision was monitored in two distinct ways. One way involved graphic visualization with locally developed programs to check the uniformity of the coverage of grid points over the surface. Another way involved comparisons to calculations with a smaller number of 194 surface points and to calculations with the cavity origin shifted by ∼0.2 Å. In most cases the reaction field results are reported to 0.1 kcal/mol and are believed precise to ∼0.2 kcal/mol or better. However, in some of the larger clusters having highly nonspherical cavities the precision is probably lower, and is so indicated by conservatively rounding off the final results to a precision of 1 kcal/mol. In a few cases no reaction field result is reported at all because it proved impossible to find any satisfactory origin from which the entire cavity interior could be seen. For molecules and clusters in solution, results are reported for a standard state of 1 M and 298 K.

Structures

The gas phase geometry and fundamental vibrations of O_3^- are reported in Table 1. The equilibrium geometry is in accord with experiment and with that obtained in other theoretical calculations.[33−39] The calculated harmonic frequencies are also in reasonable agreement with experimentally observed results. The accuracy is certainly quite satisfactory for the present purposes, where vibrational frequencies are required only to determine enthalpy and entropy contributions at 298 K to the electronic energies calculated at 0 K.

TABLE 1: Structure and Fundamental Vibrations of Gas Phase O_3^-

parameter	calculated[a]	experiment
R_{O-O} (Å)	1.357	1.36 ± 0.02[b]
O_{O-O-O} (deg)	115.5	111.8 ± 2.0[b]
ν_1 sym str (cm^{-1})	1056	975 ± 10[c]
v_2 bend (cm^{-1})	588	590 ± 10[c]
ν_3 asym str (cm^{-1})	893	796[d], 880 ± 50[b]

[a] B3LYP/6-31+G*, this work. [b] From indirect fitting to photodissociation data, ref 15. [c] From indirect fitting to photodissociation data, ref. 12. [d] From direct IR observation in Ne matrix, ref 32.

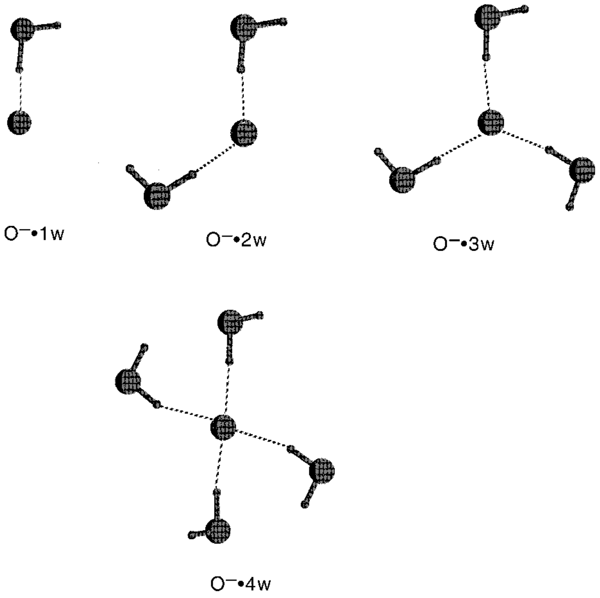

Figure 1. Calculated structures of O^-•*n*w clusters.

Structures were also determined for clusters corresponding to the entities O^-•*n*w and O_3^-•*n*w, with $n = 1-4$ and w being a shorthand notation for H_2O. In each case $n = 4$ turned out to be as many explicit water molecules as could be strongly hydrogen bonded in the first solvation shell. Considerable searching was carried out among many conceivable candidate structures in an attempt to exhaustively locate all local minima, with the proviso that each water molecule must be directly hydrogen bonded with the central O^- or O_3^- moiety of interest. No significant hydrogen bonding structures were found or expected for neutral nonpolar O_2 interacting with water molecules. The structures found for O^-•*n*w and O_3^-•*n*w are depicted in Figures 1 and 2, respectively.

For O^-•*n*w, only one local minimum structure was found for each *n*. The hydrogen bonded water molecules all tended to lie in the nodal plane of the unpaired p-electron that is localized on O^-, although some deviation from strict planarity was found with $n = 4$. The O^-•1w cluster has been the subject of a number of previous theoretical investigations, which have recently[40] been added to and summarized. The present results are consistent with the best results given there. It was pointed out[40] that use of "pure" DFT methods (i.e., methods which do not incorporate Hartree−Fock exchange integrals) gives rise to a spurious minimum-energy configuration which can best be described as elongated hydrogen peroxide anion. Hybrid DFT and correlated ab initio methods do not find a minimum at this configuration. One report[41] has been made of O^-•2w and O^-•3w; however, it describes clusters consisting of water and the just-mentioned

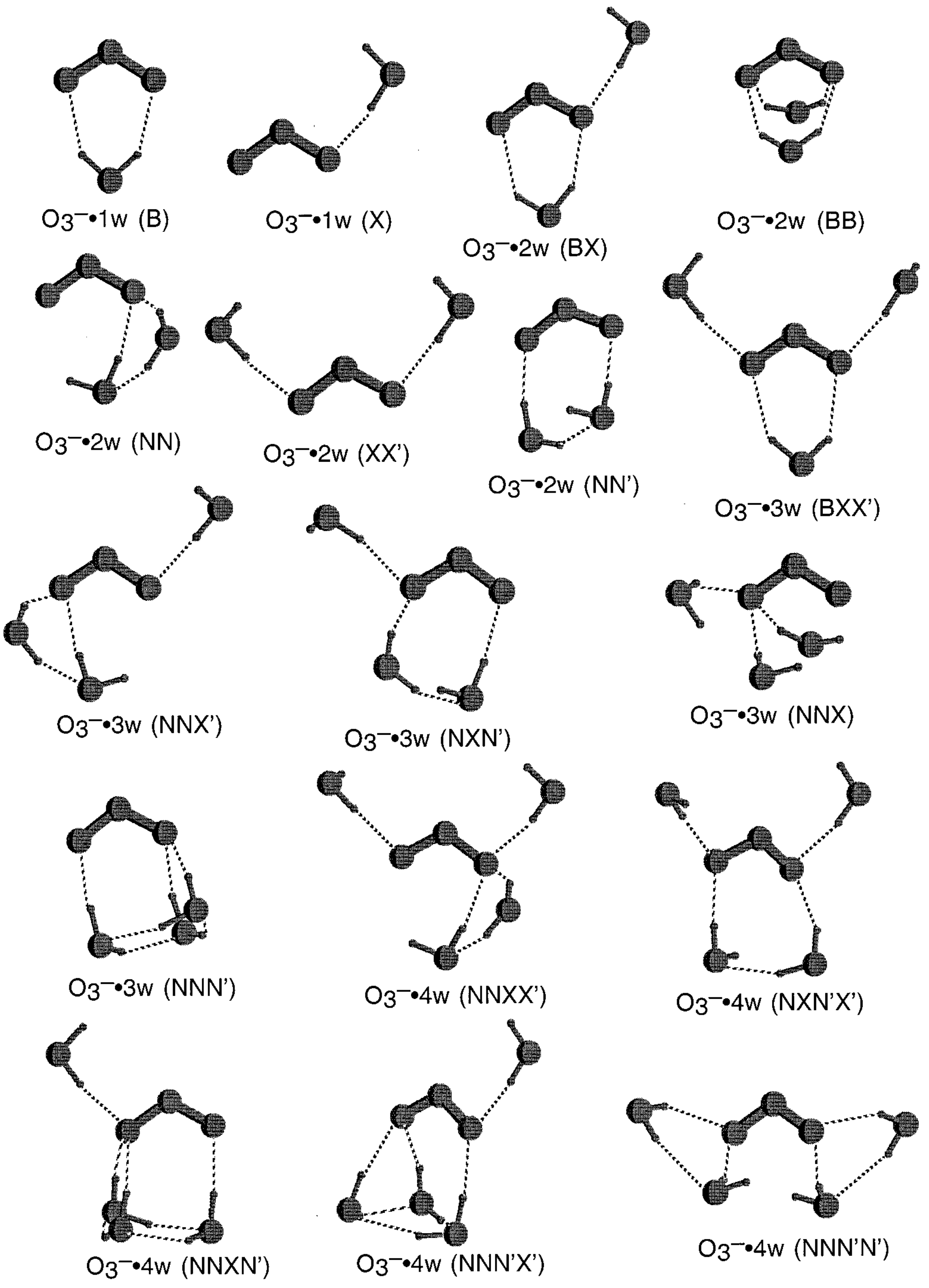

Figure 2. Calculated structures of O_3^-·*n*w clusters.

hydrogen peroxide anion, and we do not consider it reliable or relevant for the present purposes.

For O_3^-·*n*w, two or more local minimum structures were found for each *n*. No hydrogen bond to the central oxygen atom was ever found, presumably due to the fact that the central oxygen is essentially neutral, while the negative charge is divided between the terminal oxygens. The various isomers are distinguished by a notation indicating water molecules that coordinate to both terminal oxygens in a bridge (B) and water molecules that coordinate to only one terminal oxygen in roughly an endo (N) or exo (X) orientation. A prime notation distinguishes water molecules that coordinate to different terminal oxygens from those that coordinate to the same terminal oxygen. The water molecules perturb the O_3^- geometry by changing R_{O-O} up to ±0.03 Å and by changing θ_{O-O-O} up to 2°, nearly always decreasing its value. In the various clusters the value of ν_2 increases by 15−48 cm^{-1}, ν_1 decreases or increases by up to 30 cm^{-1}, and ν_2 increases by 4−43 cm^{-1} as compared to O_3^- itself.

Hydrogen Bond Energies in Clusters

Cumulative hydrogen bond energies are defined here as the energy changes for the process of assembling all the separate fragments, e.g.

$$O_3^- + nH_2O \rightarrow O_3^-\cdot n\mathrm{w}$$

and similarly for O^- and F^- (see below) clusters. Here ΔE_0^{n} corresponds to the electronic energy difference at 0 K and with all nuclei clamped in their equilibrium positions, including corrections for BSSE. ΔH_{298}^{n} and ΔG_{298}^{n} further include ap-

TABLE 2: Calculated B3LYP/6-31+G* Hydrogen-Bond Energies of Isolated $F^-\cdot n$w Clusters, Given in kcal/mol[a]

cluster	ΔE_0^n	ΔH_{298}^n	ΔG_{298}^n
$F^-\cdot$1w	−27.7	−27.9 (−23.3)	−21.3 (−18.1)
$F^-\cdot$2w	−48.9	−47.2 (−39.9)	−34.4 (−29.1)
$F^-\cdot$3w	−66.2	−62.0 (−53.6)	−38.5 (−36.7)
$F^-\cdot$4w	−80.7	−74.3 (−67.1)	−43.1 (−42.2)
$F^-\cdot$5w	−92.3	−83.7 (−80.3)	−43.3 (−46.3)

[a] Experimental results from ref 43 using high-pressure mass spectrometry are included in parentheses.

TABLE 3: Calculated B3LYP/6-31+G* Hydrogen-Bond Energies of Isolated $O^-\cdot n$w and $O_3^-\cdot n$w Clusters, Given in kcal/mol

cluster	ΔE_0^n	ΔH_{298}^n	ΔG_{298}^n
$O^-\cdot$1w	−26.3	−27.4	−21.0
$O^-\cdot$2w	−47.5	−46.8	−33.2
$O^-\cdot$3w	−64.6	−62.0	−40.9
$O^-\cdot$4w	−78.2	−73.0	−41.5
$O_3^-\cdot$1w (X)	−15.9	−14.5	−7.4
$O_3^-\cdot$1w (B)	−18.2	−16.5	−8.4
$O_3^-\cdot$2w (NN′)	−32.2	−28.5	−11.2
$O_3^-\cdot$2w (XX′)	−29.5	−26.3	−11.3
$O_3^-\cdot$2w (NN)	−31.9	−28.3	−11.3
$O_3^-\cdot$2w (BB)	−31.4	−28.1	−11.4
$O_3^-\cdot$2w (BX)	−31.6	−28.3	−13.1
$O_3^-\cdot$3w (NNN′)	−46.6	−40.4	−12.7
$O_3^-\cdot$3w (NNX)	−43.8	−38.5	−12.9
$O_3^-\cdot$3w (NN′X)	−44.3	−38.9	−14.0
$O_3^-\cdot$3w (NNX′)	−43.7	−38.5	−14.2
$O_3^-\cdot$3w (BXX′)	−43.2	−38.2	−16.1
$O_3^-\cdot$4w (NNN′N′)	−54.4	−47.2	−12.7
$O_3^-\cdot$4w (NNN′X′)	−57.1	−49.3	−14.4
$O_3^-\cdot$4w (NNXN′)	−57.4	−49.6	−14.6
$O_3^-\cdot$4w (NXN′X′)	−54.5	−47.5	−16.0
$O_3^-\cdot$4w (NNXX′)	−53.9	−47.0	−16.3

propriate contributions for a standard state of 1 atm and 298 K to the enthalpy and Gibbs free energy, respectively, arising from translational, rotational, and vibrational degrees of freedom. The simple ideal gas, rigid rotor, and harmonic oscillator models used for the latter thermodynamic contributions are expected to be satisfactory in most cases, except perhaps for the Gibbs free energies of the larger clusters where the neglect of anharmonicities in the several very low frequency vibrational modes can lead to significant errors in the calculated entropies. Such anharmonicities will generally lower the frequencies from their harmonic values, thus increasing the entropies and ultimately making the Gibbs free energies more negative than reported. This error will generally become larger as the cluster grows larger.

As one point of reference for assessing computational errors, we note that BSSE-corrected results calculated with B3LYP/6-31+G* for the water dimer give $\Delta E_0^{\text{H-bond}} = -5.3$ kcal/mol, $\Delta H_{298}^{\text{H-bond}} = -3.4$ kcal/mol, and $\Delta G_{298}^{\text{H-bond}} = 3.1$ kcal/mol, all in good agreement with the respective experimental results[42] of −5.4 ± 0.7, −3.6 ± 0.5, and 1.9 ± 0.9 kcal/mol.

The magnitudes of the errors involved in the present calculations can be better estimated by applying the same methods to an anionic water cluster system for which full experimental results are available. Such data are presented in Table 2 for the fluoride anion complexed by up to five water molecules. Experimental values for ΔH_{298}^n and ΔG_{298}^n have been obtained[43] using high-pressure mass spectrometry. The present calculations are seen to overestimate the strength of the hydrogen bonding for small clusters, and underestimate it for large clusters. The average absolute difference between calculated and experimental ΔH_{298}^n for the various clusters is 6.2 kcal/mol, but for the largest cluster the calculation is just 3.4 kcal/mol more negative than experiment. The errors are more uniform for ΔG_{298}^n, where the average absolute difference between calculation and experiment is only 2.8 kcal/mol, and for the largest cluster the calculation is 3.0 kcal/mol more positive than experiment.

Values of the cumulative hydrogen bond energies calculated for $O^-\cdot n$w and $O_3^-\cdot n$w clusters are reported in Table 3. For ozonide clusters, which all have more than one isomer for a given number of bound water molecules, isomers of the same *n* are arranged according to their calculated total free energy, with the most stable listed last.

For $O^-\cdot n$w clusters the only experimental estimate available for comparison is to the value quoted[13] for $O^-\cdot$1w as $\Delta H_{298}^1 = -26.4 \pm 4.0$ kcal/mol, and attributed to a photoelectron study,[44] which is in good agreement with our calculated value of −27.4 kcal/mol.

For $O_3^-\cdot n$w clusters the only available experimental comparison is to reported[5] incremental values of ΔG_{296}^n for $n = 1-2$ and for $n = 2-3$. We shall compare these to our calculated values between the isomers of lowest calculated total free energy. With $n = 1-2$ the experimental value is −6.2 kcal/mol, in fair agreement with the calculated value of −4.7 kcal/mol. With $n = 2-3$ the experimental value is −4.5 kcal/mol, again in fair agreement with the calculated value of −3.1 kcal/mol. These errors are substantially lower than found for the corresponding $F^-\cdot n$w clusters.

We now examine the trends in Table 3. Both O^- and O_3^- are seen to bind their first water molecule very strongly, their second water molecule somewhat less strongly, and so on. Note also that O^- binds any given number of water molecules more strongly than does O_3^-, presumably due to its more highly localized negative charge.

Bond Dissociation Energy

Hydrogen Bonding Effects. Full results of the calculated BDEs are included in Table 4. Comparison to experiment is possible only in the gas phase. The NIST Chemistry WebBook compilation[13] quotes two values for the heat of formation of O^- and two values for O_3^-. Putting these together in all permutations leads to experimental values for $\Delta H_{298}^{\text{BDE}}$ of 38.93, 39.94, 40.49, and 41.50 kcal/mol. Our calculated gas phase value of $\Delta H_{298}^{\text{BDE}} = 40.4$ kcal/mol falls comfortably in the midst of these experimental values. The calculation is also in good agreement with the value 39.86 kcal/mol that is obtained by assembling the purportedly most precise experimental values, which include a very recent determination of the heat of formation of ozone,[45] the ozone electron affinity,[14,15] the heat of formation of O atom,[46] and the O atom electron affinity.[47] This establishes that the theoretical method selected here performs very well for the gas phase BDE.

We now consider columns 3−5 of Table 4 which report BDE values for the isolated clusters. We list $\Delta E_0^{\text{BDE(H-bond)}}$, $\Delta H_{298}^{\text{BDE(H-bond)}}$, and $\Delta G_{298}^{\text{BDE(H-bond)}}$ for the process

$$O_3^-\cdot n\text{w} \rightarrow O_2 + O^-\cdot n\text{w}$$

that describes the effect of hydrogen bonding with explicit first-shell water molecules. Note that the fluctuations of values among various ozonide isomers having the same *n* is generally much smaller than the substantial decrease in BDE with increasing *n*. $\Delta E_0^{\text{BDE(H-bond)}}$ drops by about 24 kcal/mol from its gas phase value to become about 17 kcal/mol upon completion of the first

TABLE 4: Calculated Ozonide Bond Dissociation Energies, Given in kcal/mol

n	O_3^-·nw isomer	$\Delta E_0^{\mathrm{BDE(H-bond)}}$	$\Delta H_{298}^{\mathrm{BDE(H-bond)}}$	$\Delta G_{298}^{\mathrm{BDE(H-bond)}}$	$\Delta G_{298}^{\mathrm{BDE(dielec)}}$	$\Delta G_{298}^{\mathrm{BDE(aq)}}$
0		40.7	40.4	32.8	−12.8	21.9
1	X	30.3	27.5	19.2	−7.6	13.5
	B	32.6	29.6	20.2	−11.7	10.4
2	NN′	25.4	22.2	10.8	−9.2	3.5
	XX′	22.7	20.0	10.9	−6	7
	NN	25.1	21.9	10.8	−9.0	3.8
	BB	24.6	21.8	11.0	−10.5	2.4
	BX	24.8	22.0	12.6	−7.8	6.7
3	NNN′	22.7	18.9	4.6	−10.0	3.5
	NNX	19.9	16.9	4.8	−7.2	0.5
	NXN′	20.4	17.4	5.9	−6.4	1.4
	NNX′	19.8	16.9	6.1	−9	1
	BXX′	19.3	16.7	8.0	−8	2
4	NNN′N′	16.8	14.6	4.0	−6	0
	NNN′X′	19.5	16.6	5.7		
	NNXN′	19.8	16.9	5.9	−6.4	1.4
	NXN′X′	16.9	14.9	7.3		
	NNXX′	16.3	14.4	7.6		

solvation shell of four strongly hydrogen bonded water molecules. The analogous drop for $\Delta H_{298}^{\mathrm{BDE(H-bond)}}$ is about 25 kcal/mol to become about 15 kcal/mol for $n = 4$. $\Delta G_{298}^{\mathrm{BDE(H-bond)}}$ drops by about 25 kcal/mol to final values in the range of 4−8 kcal/mol both for O_3^-·3w and O_3^-·4w clusters. Based on the above comparisons of calculations to experiment, the individual O^-·nw and O_3^-·nw cluster formation steps are believed to be obtained here to an accuracy of about 3 kcal/mol or better in most cases. Building the clusters is expected to involve systematic errors that will somewhat cancel when taking differences to obtain the BDE, suggesting that the accuracy of the BDEs is itself on the order of 3 kcal/mol or less.

The clear qualitative conclusion at this point is that there is a considerable drop in the ozonide BDE due to the stronger hydrogen bond forming power of O^- as compared to O_3^-. Roughly half of this large drop is already obtained with $n = 1$, roughly another quarter upon passing on to $n = 2$, and progressively smaller contributions are made to the drop on passing to $n = 3, 4$.

Bulk Dielectric Contributions. We now consider the reaction field effect of bulk dielectric. Since the hydrogen bonding energy of each first-shell water molecule to O^- and to O_3^- is stronger that the bulk water−water hydrogen bond energy, it is reasonable to assume that all the clusters considered here will largely retain their structural integrity upon insertion into bulk water. Thus, we can make the simplifying assumption that geometry reoptimization in the bulk is unnecessary and simply calculate dielectric interactions on clusters held at their already characterized geometries. If this assumption were false, one telling sign would be to find considerably different dielectric contributions to the various O_3^-·nw isomers having the same n, but this turns out not to be the case, thus giving support to the assumption.

Our current implementation of reaction field theory[28] only allows calculations at the Hartree−Fock level, and use of this here requires some comment. The reaction field energies of O^- and O_3^- are strongly dominated by the interaction of the bulk with the net charge of the solute. Values in the range from −55 to −81 kcal/mol (see below) that are found here are an order of magnitude larger than typical free energies of solvation for small neutral solutes. Therefore, any electronic structure method that correctly describes the distribution of the net negative solute charge should be suitable for the dielectric determination. Detailed rearrangements due to electron correlation will make little change in the overall solute density and so have small effect on the reaction field. Thus, we believe that the UHF/6-31+G* method used here to estimate bulk dielectric effects should be quite satisfactory for the present purposes. These contributions will simply be added to the first-shell hydrogen bond effects already determined above by other methods more suitable for that aspect.

The cavity shape is defined in considerable detail by mapping out a solute electronic isodensity contour. It has been previously recommended[29] that the value $0.001e/a_0^3$ be chosen for the contour in order to determine bulk electrostatic contributions. This leads to a dielectric contribution to the free energy of solvation $\Delta G_{298}^{\mathrm{dielec}}$ of −80.6 kcal/mol for O^- and of −68.0 kcal/mol for O_3^-. Choosing a significantly larger cavity based on the $0.0005e/a_0^3$ contour or a significantly smaller cavity based on the $0.002e/a_0^3$ contour changes the above O^- result by a little over 6 kcal/mol either way and changes the above O_3^- result by a little under 3 kcal/mol either way, but these largely cancel in forming the BDE which is only affected by a little over 2 kcal/mol either way. Spot checks indicated that the BDEs of ozonide−water clusters were even less sensitive than this, usually changing less than 2 kcal/mol either way over this same wide range of isodensity contour values. Henceforth we define the cavity by adopting the recommended value[29] of $0.001e/a_0^3$ for the isodensity contour and estimate an error contribution to the BDE of about 1 kcal/mol from uncertainty in the precise cavity size.

A unique aspect of our reaction field implementation is inclusion of volume polarization effects[27−31] arising from penetration of solute charge outside the cavity. This effect makes significant contributions of −8.7 and −8.3 kcal/mol in the above quoted values of $\Delta G_{298}^{\mathrm{dielec}}$ for O^- and O_3^-, respectively. The net effect of volume polarization on the BDE is therefore only a few tenths of a kilocalorie per mole in this case, but it becomes as large as 1 kcal/mol or more for some of the larger clusters and so is routinely included here.

The value calculated for $\Delta G_{298}^{\mathrm{dielec}}$ of the neutral nonpolar O_2 molecule is very small, only −0.1 kcal/mol. For O^-·nw clusters, values of $\Delta G_{298}^{\mathrm{dielec}}$ range from −72.1 to −60.7 kcal/mol, while for O_3^-·nw clusters they range from −64.5 to −54.9 kcal/mol.

For each cluster we report in column 6 of Table 4 the calculated dielectric contribution to the BDE, except that no results are given for several O_3^-·4w isomers which are very nonspherical and do not contain an appropriate origin for the single center expansion of our reaction field calculation. It is seen that the bulk dielectric contributions from $\Delta G_{298}^{\mathrm{dielec}}$ significantly lower the BDE for each cluster, although this effect is secondary in importance to the explicit formation of first-shell hydrogen bonds. These dielectric contributions do not vary as strongly with n as do the hydrogen bonding contributions, and in fact are changing only very slowly with n for the larger clusters. With $n = 2$ the dielectric contributions are all in the range of about -8.3 ± 2.2 kcal/mol and with $n = 3$ in the range of about -8.2 ± 1.8 kcal/mol. Thus, it is reasonable to surmise that with $n = 4$ the dielectric contributions will all be in the range of about -8.0 ± 2.0 kcal/mol, which is compatible with the two known results having $n = 4$.

Net Results. These separate contributions can now be assembled to obtain values for the total BDE in aqueous solution as given by

$$\Delta G_{298}^{\mathrm{BDE(aq)}} = \Delta G_{298}^{\mathrm{BDE(H-bond)}} + \Delta G_{298}^{\mathrm{BDE(dielec)}} + RT \ln(\rho_{\mathrm{soln}}/\rho_{\mathrm{gas}})$$

Here the factor $RT \ln(\rho_{\mathrm{soln}}/\rho_{\mathrm{gas}}) = 1.89$ kcal/mol representing the solute's density change between gas and solution is a consequence of altering the standard state convention of 1 atm that was adopted for $\Delta G_{298}^{\mathrm{BDE(H-bond)}}$ to the convention of 1 M that is appropriate for solution.

Results for the total calculated aqueous BDEs are given in the final column of Table 4. Here again the spread of values for isomers of the same n is generally smaller than the overall change upon incrementing n. For the most stable $n = 3$ cluster we see that $\Delta G_{298}^{\mathrm{BDE(aq)}}$ is 2 kcal/mol. If, as discussed above, we estimate bulk dielectric contributions of -8.0 ± 2.0 kcal/mol for the uncharacterized $n = 4$ clusters, we would obtain $\Delta G_{298}^{\mathrm{BDE(aq)}}$ values of -0.6 ± 2.0 kcal/mol for the NNN′X′ isomer, 1.0 ± 2.0 kcal/mol for the NXN′X′ isomer, and 1.3 ± 2.0 kcal/mol for the most stable NNXX′ isomer. Thus, the most stable $n = 4$ cluster could have $\Delta G_{298}^{\mathrm{BDE(aq)}}$ as much as 1 kcal/mol more endothermic than the most stable $n = 3$ cluster. Incorporating this 1 kcal/mol as an additional contribution to the error estimate, we conclude that the most stable $n = 3$ and $n = 4$ clusters give similar final results and are consistent with an estimate of about 2 ± 4 kcal/mol for the free energy of aqueous ozonide bond dissociation.

The effects of water in this system are dominated by electrostatic interactions with the ionic solutes. Electrostatic interactions should be treated very well for the anions with first-shell water molecules by the quantum mechanical calculations on clusters, and reasonably well for the anions and for O_2 with the remaining bulk by the dielectric continuum calculations. However, nonelectrostatic cavitation and van der Waals interactions, even though generally smaller in magnitude and of much shorter range than electrostatic interactions, are probably not negligible. Nonelectrostatic interactions are treated only partially for the anions with first-shell water molecules by the quantum mechanical calculations on clusters, and are not treated at all for the anions or for O_2 with the remaining bulk in any of the calculations.

The nonelectrostatic (nonelec) interactions are readily approximated[48] by replacing the anions by neutral, nonpolar molecules of the same size and shape, for which the electrostatic component is negligible. Thus, in the present case we may take $\Delta G^{\mathrm{nonelec}}(O_2) \approx \Delta G^{\mathrm{solv}}(O_2)$ directly and estimate $\Delta G^{\mathrm{nonelec}}(O_3^-) \approx \Delta G^{\mathrm{solv}}(O_3)$ and $\Delta G^{\mathrm{nonelec}}(O^-) \approx \Delta G^{\mathrm{solv}}(\mathrm{Ne})$. Using experimental data[49] for these free energies of solvation, the full nonelectrostatic contribution to the BDE is thereby estimated to be 4.0 kcal/mol. This should overestimate the actual correction to be applied, because in assembling the clusters some (unknown) fraction of the cavitation, repulsion, and dispersion interactions between the anions and water is accounted for by the calculated interactions of anions with explicit water molecules in the larger clusters. On the other hand, if the calculations on the larger clusters faithfully described all these interactions, then the nonelectrostatic correction to be applied would be just the O_2 solvation free energy[49] of 2.0 kcal/mol. The actual situation is presumably intermediate between these two limiting cases, so we empirically estimate the nonelectrostatic solvation correction to be applied to our calculated BDE as 3 ± 1 kcal/mol. Putting this together with our best fully theoretical result obtained above finally leads to a semitheoretical estimate of 5 ± 5 kcal/mol for $\Delta G_{298}^{\mathrm{BDE(aq)}}$.

Conclusion

The present work verifies that there is indeed a considerable lowering of the ozonide $\Delta G_{298}^{\mathrm{BDE(aq)}}$ in aqueous solution over that in the gas phase by about 20 kcal/mol. The most important reason for this is that the more localized negative charge in O^- allows it to make stronger hydrogen bonds with first-shell water molecules than does O_3^-. Roughly half of this effect is obtained with just one explicit water molecule, and progressively smaller contributions come from additional water molecules that make up the first solvation shell. A secondary but still quite significant reason for the lowering comes from the smaller cavity formed by O^- and its first-shell water clusters leading to a larger reaction field stabilization from the bulk dielectric than for O_3^- and its analogous first-shell water clusters. Combining both effects and taking the most stable isomers of the larger clusters treated as being the most realistic, we obtain a fully theoretical estimate of $\Delta G_{298}^{\mathrm{BDE(aq)}} \approx 2 \pm 4$ kcal/mol for the free energy of aqueous ozonide bond dissociation.

Electrostatic contributions to solvation free energy need to be supplemented by contributions for cavity formation and for repulsion and dispersion interactions between solute and solvent. These nonelectrostatic effects are not very well represented in our calculations. We have therefore obtained an independent empirical estimate of the nonelectrostatic contributions. Including this leads to our best semitheoretical prediction that $\Delta G_{298}^{\mathrm{BDE(aq)}} \approx 5 \pm 5$ kcal/mol. The indicated uncertainty, which combines estimates of the accuracy of the calculations and of the empirical correction, is substantial but still much smaller than the effect we are attempting to describe. This enables us to draw the qualitative conclusion that the free energy of ozonide bond dissociation is small and probably endothermic in water.

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