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Article

Accurate Computational Model for the Hydration Extent of Atmospherically Relevant Carbonyls on Aqueous Atmospheric Particles

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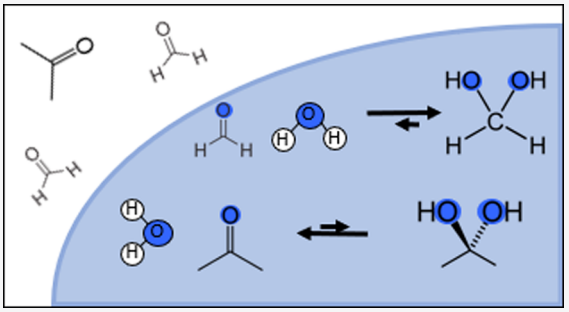
ABSTRACT: The carbonyl hydration equilibria of several atmospherically relevant carbonyl compounds were studied using nuclear magnetic resonance (NMR) spectroscopy and computationally investigated using the MG2MS electronic structure method. The results were used to build an empirically adjusted computational model that resulted in the calculation of free energies of hydration that were accurate to within 1 kcal mol^{-1}. The new model was used to predict the hydration extent of other potentially atmospherically relevant carbonyl compounds for which no experimental data exists. Because the hydration extent of a carbonyl compound dramatically affects its effective volatility and Henry's law solubility, the more accurate estimates for the extent of carbonyl hydration predicted by this new model will help improve our understanding of which carbonyl compounds are major constituents of aqueous atmospheric particles.



KEYWORDS: *atmosphere, aerosol, carbonyl, hydration, equilibrium*

INTRODUCTION

Secondary organic aerosol (SOA)[1] forms in the atmosphere via gas-particle partitioning. SOA chemical composition can also be affected by in-particle chemical processing of condensed components. The particular chemical makeup of SOA likely plays a role in the effect that it has on human respiratory and cardiovascular diseases,[2,3] visibility loss,[4] and climate modification.[5] To help predict the occurrence of different atmospheric constituents on atmospheric particles such as SOA and clouds, attention has been focused on parameterizing these constituents with respect to their volatility and Henry's law solubility, which is relevant to their interaction with aqueous atmospheric particles.[6] Although many carbonyl compounds are directly emitted into the atmosphere by natural and anthropogenic sources,[7] the oxidizing nature of the atmosphere is also capable of installing carbonyl functional groups into almost any organic compound, including the dominant nonmethane hydrocarbon, isoprene.[8] Given their ubiquitous presence in the atmosphere, it is important to understand the physical and chemical properties of these carbonyl compounds present in the atmosphere under various atmospheric conditions, including their interactions with aqueous atmospheric particles.

Carbonyl compounds, like propionaldehyde, are capable of undergoing nucleophilic addition of water across the carbonyl double bond to form hydrated geminal diol species (Figure 1).[9]

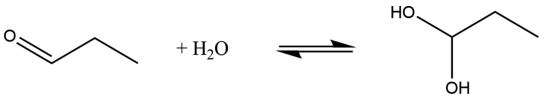


Figure 1. Hydration equilibrium for propionaldehyde, a known atmospheric constituent.

This hydration process dramatically affects both the volatility and Henry's law solubility of propionaldehyde in aqueous solutions. The EPA's chemical and physical property calculator, EPISUITE, predicts that the hydrated form of propionaldehyde is almost 300 times less volatile and 20 times more water-soluble than the unhydrated form[10] owing to the strong effect of the two hydrogen-bonding groups in the hydrated form. This clearly illustrates that the ability of a particular carbonyl compound to undergo hydration significantly increases the probability that it will be incorporated into aqueous atmospheric particles. However, the propensity of a particular compound to undergo hydration can vary enormously—while formaldehyde exists almost entirely in

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the hydrated form under aqueous conditions,[11] acetone remains almost entirely unhydrated.[12]

There have been several previous experimental and computational studies of the hydration of potentially atmospherically relevant carbonyl compounds.[13−20] However, these studies have focused on parameterizing the properties of a subset of chemical species for a particular atmospheric system, as opposed to developing qualitative general structure−property relationships or quantitatively predictive models for carbonyl hydration. We conducted temperature-dependent measurements of the hydration equilibrium constant for several simple atmospherically relevant carbonyl compounds to establish the van't Hoff thermodynamic parameters using nuclear magnetic resonance (NMR). We then used these results, and other experimental measurements of the free energy of hydration, to empirically calibrate MG2MS ab initio electronic structure calculations and create a quantitative model that accurately predicts free energies of hydration. We also used MG2MS results to assess the accuracy of group contribution thermodynamic methods for carbonyl hydration reactions. Finally, the calibrated computed hydration properties were used to establish structure free energy of hydration relationships and predict the hydration extent of a number of potentially atmospherically relevant carbonyl compounds for which experimental data is lacking.

MATERIALS AND METHODS

Chemicals. The following commercially available chemicals were used from MilliporeSigma (acetaldehyde, 99.5%; propionaldehyde, 97%; pyruvic acid, 98%; methylglyoxal solution, 40% in H_2O; acetone, 99.5%; hydroxyacetone, 90%; 2,3-butanedione, 97%), TCI America (dihydroxyacetone, 97%), and Cambridge Isotope Laboratories, Inc. (deuterium oxide, 99.5%). The potassium salts of 1-sulfatoacetone and 3-sulfato-1-hydroxyacetone were each prepared and characterized according to the procedure outlined by Hettiyadura et al.[21]

Hydration Equilibrium Constant Measurements. All systems were investigated in bulk solutions with total volumes of 750 μL (the amount required for NMR analysis) with either 10 or 50 μL (or 10 mg of the appropriate potassium salt of the sulfato compounds) of the carbonyl compound added to an appropriate volume of D_2O. The systems were observed to achieve equilibrium within the 5 min preparation and NMR measurement time frame. This fast establishment of equilibrium is consistent with previous measurements of short hydration lifetimes ($\tau_{hydration}$ < 30 s) for formaldehyde,[22] glycoaldehyde,[23] glyoxylic acid,[22] and pyruvic acid.[24] NMR spectra were collected on a Bruker 400 MHz instrument using built-in pulse sequences. ^{1}H spectra were calibrated to the HDO peak at 4.79 ppm. The relative concentrations of the various species were determined by integration of one or more unique peaks in the ^{1}H spectra. The overall precision of the relative concentration ratios was estimated to be better than 10% (with much better precisions for systems with K_H near-unity). van't Hoff data was collected by performing temperature-dependent measurements of the concentration ratios. The built-in Bruker temperature control apparatus was used to vary the temperatures from 298 to 318 K. A relatively narrow temperature range was used to prevent loss of volatile components and thermal degradation of unstable compounds.

Computations. The van't Hoff parameters for the hydration equilibria of potentially atmospherically relevant carbonyl compounds were calculated according to the following procedure. Geometries (determined at the B3LYP/6-31G(d,p) level) and energies of the relevant species were calculated using a modified version of the G2MS compound method (MG2MS),[25] a variation on the G2 theory.[26] The polarizable continuum model (PCM) method[27] was used to account for the effects of water solvation on the reactant and product properties. All calculations were carried out with the Gaussian 09 computational suite.[28] Each stationary point was confirmed as a potential energy minimum by inspection of the calculated frequencies. The overall energy expression for the MG2MS scheme is defined in eq 1

$$E_{elec}(0\ K) = E_{CCSD(T)/6-31G(d)} + E_{MP2/6-311+G(2df,2p)} - E_{MP2/6-31G(d)} + HLC \quad (1)$$

where HLC is an empirically defined correction term with HLC = $An_\alpha + Bn_\beta$, where n_α and n_β are the number of α- and β-electrons, respectively, and the constants A and B are 6.06 and 0.19 mH, respectively (all species investigated were closed shell; therefore $n_\alpha = n_\beta$). The enthalpy is calculated from eq 2

$$H(298\ K) = E_{elec}(0\ K) + E_{zpe} + E_{thermal} \quad (2)$$

where E_{zpe} is the zero point energy and $E_{thermal}$ includes the corrections to necessarily adjust the internal energy to 298 K and convert to enthalpy. The free energy is calculated from eq 3

$$G(298\ K) = H(298\ K) - 298\ K \times S(298\ K) \quad (3)$$

where S(298 K) is the entropy calculated at 298 K.

Our previous MG2MS results for atmospherically relevant systems (including radicals and ions) indicate that the MG2MS calculated enthalpies of reaction are typically accurate to within 2 kcal mol^{-1} for systems similar to those under study here.[29]

The MG2MS free-energy results were observed to be systematically in error for compounds for which experimental values are available. To correct for this error, two methods were used to empirically adjust the MG2MS results to achieve more accurate predictions for compounds that have not been experimentally studied. The first method involved using the experimental van't Hoff parameters to determine an MG2MS correction factor for the enthalpy and entropy of hydration individually. The second method involved determining an MG2MS correction factor for the free energy of hydration at 298 K, which was possible because many more experimental 298 K free energy of hydration values are available. The advantage of the first method is that it should lead to more accurate predictions for the free energy of hydration at temperatures other than 298 K, while the advantage of the second method is that it should be better calibrated to experimental values and lead to more accurate predictions for the free energy of hydration at 298 K.

RESULTS AND DISCUSSION

NMR Assignments. As an example of the typical NMR spectra collected for the hydration of carbonyl compounds, the ^{1}H NMR spectrum and assignments for the species present in the propionaldehyde hydration system are given in Figure 2. Because the hydration of the carbonyl carbon atom causes significant changes in the electron density experienced by the nearby hydrogen atoms, large chemical shift changes are

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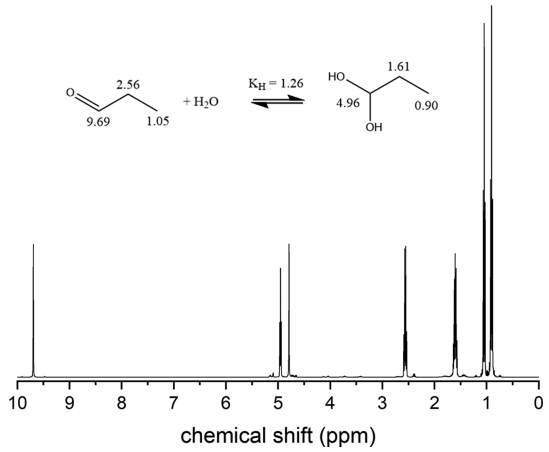

Figure 2. ^{1}H NMR spectrum for the propionaldehyde hydration system at 298 K.

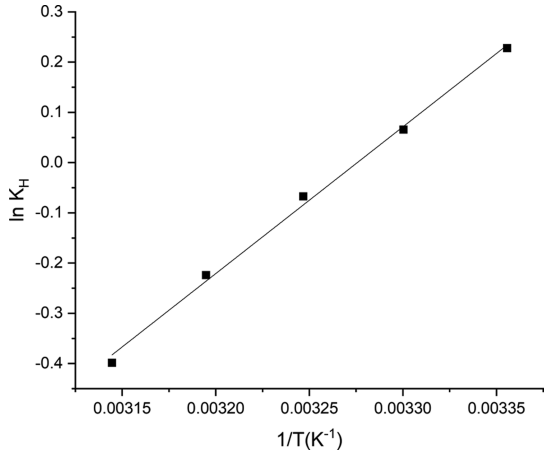

Figure 3. van't Hoff plot for the propionaldehyde hydration system. The corresponding thermodynamic values (and associated uncertainties) are given in Table 1.

associated with the hydration of carbonyls and the identification and quantification of all species are straightforward.

Experimental Thermodynamic Parameters. The hydration equilibrium constants were calculated directly from the NMR-determined concentration ratio of the hydrated compound to the carbonyl compound. For example, for the propionaldehyde hydration system, K_H is defined as

$$K_H = \frac{[CH_3CH_2CH(OH)_2]}{[CH_3CH_2C(=O)H]} \quad (4)$$

The standard free energies of hydration were directly determined from the hydration equilibrium constants measured at T = 298 K

$$\Delta_r G^\circ = -RT \ln K_H \quad (5)$$

The van't Hoff parameters were determined via linear regression analysis from measurements of the temperature dependence of the equilibrium constant

$$\ln K_H = \frac{-\Delta_r H^\circ}{R} \times \frac{1}{T} + \frac{\Delta_r S^\circ}{R} \quad (6)$$

Figure 3 shows the van't Hoff plot resulting from experimental measurements for propionaldehyde. In this ideal case where K_H is near-unity, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ were determined with only 3% (1σ) error. Table 1 contains the van't Hoff parameters (and one standard deviation uncertainties) for all systems experimentally studied in the present work. The expected uncertainty for a $\Delta_r G^\circ$ value near zero using the previously stated 10% concentration uncertainties is about 0.1 kcal mol^{-1}, which is consistent with the lowest regression analysis-determined $\Delta_r G^\circ$ uncertainties cited in Table 1. For the $\Delta_r G^\circ$ values, the present results are in very good agreement with most previous literature reports, while statistically significant differences for some of the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values are observed. The good $\Delta_r G^\circ$ agreement and subpar $\Delta_r H^\circ$ and $\Delta_r S^\circ$ agreement suggest that some of the earlier studies might have been impacted by inaccuracies in the temperature-dependent measurements and/or analysis. For example, the previous $\Delta_r H^\circ$ and $\Delta_r S^\circ$ parameters for acetaldehyde and acetone were determined from measurements at only three different temperatures.[12]

Computational Thermodynamic Model Performance. Table 1 also contains the MG2MS computational thermodynamic results for the set of presently experimentally studied carbonyl compounds, while Table S1 contains the MG2MS computational thermodynamic results for a wider set of potentially atmospherically relevant compounds. The results in Table 1 indicate that, as expected, the MG2MS $\Delta_r H^\circ$ values are within the expected 2 kcal mol^{-1} of the experimental values, with no obvious systematic error. However, large systematic error is observed for the $\Delta_r S^\circ$ values. This is likely because the MG2MS method leads to $\Delta_r S^\circ$ values that are about a factor of 2 too negative compared to the experimental results, which then leads to ΔG values that are about 5 kcal mol^{-1} too positive at 298 K. This computational systematic error has also been observed in previous ab initio electronic structure studies of the hydration of glyoxal.[13,19] Kua et al. identify problems with the treatment of translation and rotation, differing solubilities of the reaction components, and the problem of inseparability of the thermal corrections to free energy and effect of the solvent as potential reasons for the systematic error.[13] A method in which the entropy contribution to free energy is estimated as −0.5TS (i.e., half of its computed contribution) was previously shown to be effective in compensating for the systematic error.[13] While this method improved the agreement of the present computational MG2MS values with experimental values, we found that, somewhat surprisingly, a single system-independent correction factor was even more effective. In particular, we used two different models in which the MG2MS results are empirically calibrated to achieve the best agreement with available experimental results, as discussed above in the Materials and Methods section. The first model has separate correction factors for the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ terms, which are determined from the experimental van't Hoff results. For this first model, the $\Delta_r H^\circ$ MG2MS results are systematically too positive by 0.4 kcal mol^{-1}, while the $\Delta_r S^\circ$ MG2MS results are systematically too negative by 19 cal mol^{-1} K^{-1} when compared to the available experimental results (Table 1). The MG2MS results are adjusted by these constant values to achieve new, more accurate "van't Hoff-adjusted" thermodynamic values (Table S1). The second model has a single correction factor for $\Delta_r G^\circ$ determined from a larger set of experimental $\Delta_r G^\circ$ values. For this second model, the $\Delta_r G^\circ$ MG2MS results are systematically

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Table 1. van't Hoff Parameters (and One Standard Deviation Uncertainties) for Experimentally Studied Systems (Units: $\Delta_r H°$ and $\Delta_r G°$ (kcal mol^{-1}) and $\Delta_r S°$ (cal mol^{-1} K^{-1}))

	experimental, this work			experimental, literature			MG2MS, this work		
system	$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$	$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$	$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$
acetaldehyde	−6.441 ± 0.093	−21.00 ± 0.30	−0.19 ± 0.13	−5.3[12]	−17[12]	−0.2[12]	−6.0	−39	5.4
propionaldehyde	−5.80 ± 0.19	−19.01 ± 0.62	−0.14 ± 0.26			−0.1[18]	−6.0	−39	5.5
pyruvic acid	−6.021 ± 0.038	−18.84 ± 0.12	−0.407 ± 0.052	−8.2[30]	−27[30]	−0.2[30]	−6.5	−40	5.5
methylglyoxal	−7.62 ± 0.62	−26.2 ± 2.0	0.19 ± 0.87			0.2[31]	−6.9	−41	5.4
acetone	−2.64 ± 0.37	−21.3 ± 1.2	3.71 ± 0.51	−3.1[12]	−23[12]	3.7[12]	−0.4	−42	12.2
hydroxyacetone	−6.1 ± 0.34	−28.2 ± 1.1	2.27 ± 0.47			2.3[32]	−5.1	−41	7.2
dihydroxyacetone	−6.1 ± 0.70	−19.3 ± 2.3	−0.35 ± 0.98				−7.8	−42	4.7
2,3-butanedione	−5.78 ± 0.84	−16.9 ± 2.8	−0.7 ± 1.2			−0.4[33]	−4.7	−39	7.0

Table 2. $Log_{10}K_H$ Values for C_1−C_3 Compounds

	experimental	van't Hoff-adjusted	van't Hoff (adj − exp)	$\Delta_r G^{ezp}$-adjusted	$\Delta_r G^{ezp}$ (adj − exp)
C_1 compounds					
formaldehyde	3.4[11]	3.4	0.0	2.9	−0.5
sulfato formaldehyde ion		−4.7		−5.2	
C_2 compounds					
acetaldehyde	0.1[a]	0.5	0.4	0.0	−0.1
glycoaldehyde	1.0[23]	1.6	0.6	1.1	0.1
2-sulfato acetaldehyde ion		1.8		1.2	
glyoxal		3.3		2.8	
monohydrated glyoxal		3.0		2.5	
glyoxylic acid	2.5[22]	4.5	2.0	4.0	1.5
C_3 compounds					
propionaldehyde	0.0[a]	0.4	0.3	−0.1	−0.2
acetone	−2.7[a]	−4.5	−1.8	−5.0	−2.3
hydroxyacetone	−1.7[a]	−0.8	0.9	−1.3	0.4
fluoroacetone	−0.8[33]	−0.7	0.1	−1.2	−0.4
chloroacetone	−1.0[33]	0.0	1.0	−0.5	0.5
sulfatoacetone ion	−1.1[a]	−0.2	0.9	−0.7	0.4
nitratoacetone		0.1		−0.4	
1,1-dichloroacetone	0.4[33]	1.0	0.6	0.5	0.1
dihydroxyacetone	0.3[a]	1.1	0.8	0.5	0.2
1,3-dichloroacetone	0.6[33]	1.5	0.9	1.0	0.4
3-sulfato-1-hydroxyacetone ion	0.0[a]	0.5	0.5	0.0	0.0
lactaldehyde	1.4[35]	1.7	0.3	1.2	−0.2
methylglyoxal (1)		2.8		2.3	
methylglyoxal (2)		1.2		0.7	
monohydrated (1) methylglyoxal	−0.2[31]	0.6	0.8	0.0	0.2
pyruvic acid	0.1[30]	0.6	0.5	0.1	0.0

[a]This work.

too positive by 5.4 kcal mol^{-1} (Table S1). Therefore, the MG2MS results are adjusted by this constant value to achieve new, more accurate "$\Delta_r G^{exp}$-adjusted" $\Delta_r G°$ values (Table S1). When comparing the predictions from the van't Hoff-adjusted $\Delta_r G°$ values to all available experimental $\Delta_r G°$ values, the average error is 1.0 kcal mol^{-1}, with a standard deviation of errors of 0.7 kcal mol^{-1}. When comparing the predictions from the $\Delta_r G^{exp}$-adjusted $\Delta_r G°$ values to all available experimental $\Delta_r G°$ values, the average error is 0.7 kcal mol^{-1}, with a standard deviation of errors of 0.8 kcal mol^{-1}. Therefore, the $\Delta_r G^{exp}$-adjusted model leads to slightly more accurate $\Delta_r G°$ values, but there is a slightly larger fraction of outlier values as well. However, both models lead to similar predicted values, which are significantly more accurate than the unadjusted MG2MS values and more accurate than purely computational models, which used much more computationally intensive high levels of theory.[34] Since equilibrium constants are more useful for the purpose of assessing the potential atmospheric relevance of carbonyl hydration process, Table 2 contains the experimental, van't Hoff-adjusted, difference between van't Hoff-adjusted and experimental and $\Delta_r G^{exp}$-adjusted, and difference between $\Delta_r G^{exp}$-adjusted and experimental $log_{10}K_H$ values for a number of C_1−C_3 atmospherically relevant carbonyls. Table 3 contains the same information for a number of C_4−C_7 atmospherically relevant carbonyls. All of the values in Tables 2 and 3 were calculated from the thermodynamic data reported in Table S1.

Structure Free-Energy Relationships. The $log_{10}K_H$ values (Tables 2 and 3) allow for the opportunity to assess whether there are significant structure free-energy relationships that can be used to qualitatively predict the hydration propensity of potentially atmospherically relevant carbonyl compounds. The results clearly indicate that the aldehydes generally have much larger K_H values than do the ketones, a

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Table 3. $Log_{10}K_H$ Values for C_4−C_7 Compounds

	experimental	van't Hoff-adjusted	van't Hoff (adj − exp)	Δ_rG^{ezp}-adjusted	Δ_rG^{ezp} (adj − exp)
C_4 compounds					
butanal	−0.1[12]	0.5	0.6	−0.1	0.0
2-butanone		−3.3		−3.8	
2,3-butanedione	0.3[33]	−0.6	−0.9	−1.2	−1.5
1-sulfato-2,3-butanedione ion		−0.2		−0.7	
methyl vinyl ketone	<−2.3[18]	−2.1		−2.6	
3,4-dihydroxy-2-butan-2-one (DHBO)		−1.7		−2.3	
methacrolein	<−2.3[18]	0.0		−0.5	
2,3-dihydroxy-2-methylpropanal (DHMP)		0.0		−0.5	
4-hydroxy-2-butanone		−2.6		−3.1	
4-nitrato-2-butanone		−1.9		−2.5	
4-sulfato-2-butanone ion		−2.7		−3.2	
C_5 compounds					
2-pentanone		−3.0		−3.6	
3-pentanone		−4.6		−5.1	
2-hydroxy-2-methyl-4-sulfato-3-butanone		−0.1		−0.6	
3-(hydroxymethyl)-2-methyloxirane-2-carbaldehyde (1-IEPOXO)		2.0		1.4	
3-(hydroxymethyl)-3-methyloxirane-2-carbaldehyde (4-IEPOXO)		3.1		2.6	
2,3,4-trihydroxy-2-methylbutanal (2-MT-1-aldehyde)		0.6		0.1	
2,3,4-trihydroxy-3-methylbutanal (2-MT-4-aldehyde)		−0.5		−1.1	
C_7 compound					
benzaldehyde		−1.9		−2.4	

distinction that is true of most carbonyl compounds.[9] As most clearly illustrated by acetone and its derivatives in Table 2, the present results indicate that neighboring electronegative functional groups such as other carbonyl, hydroxyl, and halogen groups serve to increase the extent of hydration, most likely by drawing electron density away from the carbonyl carbon atom, which makes for a more electropositive target for nucleophilic attack by water. This effect is quantitatively significant because acetone has a K_H value so small ($log_{10}K_H$ = −2.7) that it is difficult to experimentally measure, while several of its electronegative functional group-derivatized forms have K_H values greater than unity ($log_{10}K_H > 0$). Neighboring carbonyl groups have the largest effect on K_H values, with glyoxal and glyoxylic acid having much larger K_H values than the base compound acetaldehyde, and methylglyoxal and pyruvic acid having much larger K_H values than the base compounds propionaldehyde and acetone. With the exception of formaldehyde, neighboring sulfate and nitrate functional groups have a stronger effect than hydroxyl groups in their increasing of K_H, thus suggesting that carbonyl-containing organosulfates and organonitrates are more likely to be significantly hydrated under atmospheric conditions than multifunctional hydroxy and monofunctional carbonyl compounds.

Comparison to Group Contribution Methods. In addition to ab initio electronic structure methods, the Joback group contribution method[36] has been used to estimate the thermodynamic values of carbonyl hydration reactions.[20] This method uses the molecular structure and functional group identities of a variety of chemical species to parameterize the contribution of each structural aspect to a particular experimentally measured thermodynamic value. This approach has the benefit of a very simple and fast computational algorithm, but its accuracy is constrained by the type of molecules used to "train" the group contribution parameters. For example, this method was shown to perform extremely well, accuracies of better than 1 kcal mol^{-1}, for the prediction of the gas-phase free energies of formation of a number of atmospherically relevant carbonyl compounds, some of which were themselves used in the Joback training set.[20] Because the present study focused on the aqueous phase thermodynamic parameters, there is not a simple way to compare the present thermodynamic parameters to the gas-phase ones predicted by the Joback method. However, we have carried out separate calculations on the gas-phase hydration reaction of acetaldehyde to allow a direct comparison to the results obtained by the Joback method. While ab initio methods are often characterized by significant systematic errors, as discussed above for the calculation of Δ_rG° values for the carbonyl hydration reactions, the use of isodesmic (bond-conserving) reactions allows for the cancellation of most systematic error and can lead to highly accurate ab initio ΔG values. For example, an isodesmic reaction approach was used to calculate the free energy of formation of carbon dioxide, via the disproportionation reaction of formaldehyde to form methane and carbon dioxide, with less than 1 kcal mol^{-1} error using a level of theory significantly lower than the present MG2MS approach.[37] Since the standard gas-phase enthalpy of formation of ethylene glycol is a well-established experimental property and its standard entropy of formation can be calculated from similarly well-known experimental values,[38] an isodesmic isomerization reaction between ethylene glycol and the acetaldehyde hydration product was used to establish a value for the gas-phase free energy of formation of the acetaldehyde hydration product

$$\Delta_rG^\circ = \Delta_fG^\circ(CH_3CH(OH)_2) - \Delta_fG^\circ(CH_2(OH)CH_2(OH)) \quad (7)$$

such that

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$$\Delta_f G^\circ(CH_3CH(OH)_2) = \Delta_r G^\circ + \Delta_f G^\circ(CH_2(OH)CH_2(OH)) \quad (8)$$

The MG2MS value for $\Delta_r G^\circ$ for the isodesmic gas-phase ethylene glycol to acetaldehyde hydration product isomerization reaction was found to be −11.4 kcal mol^{-1}. Using the experimental $\Delta_f G^\circ$ value for gaseous ethylene glycol[38] of −73.1 kcal mol^{-1}, the $\Delta_f G^\circ$ value for the gaseous acetaldehyde hydration product is determined to be −84.5 kcal mol^{-1}, with an uncertainty on the order of 1 kcal mol^{-1}, as discussed above. The Joback method, using the Yaws[36] parameterization, predicts a value $\Delta_f G^\circ$ for the acetaldehyde hydration product of −74.1 kcal mol^{-1}; this large error likely results from the lack of geminal diol species thermodynamic data in the Joback training set. Therefore, while group contribution algorithms such as the Joback method are considerably easier to apply than the present empirically adjusted MG2MS method, those methods can be highly inaccurate, particularly when relatively unusual structural components such as geminal diols are present in the reaction system. Because the group contribution term for geminal diols is therefore likely in error in the Joback method and would lead to erroneous results for the hydration of any carbonyl, this method is not recommended for the prediction of the hydration extent of atmospherically relevant carbonyls.

Atmospheric Implications. As outlined in the Introduction section, the ability to accurately predict the hydration extent of atmospherically important carbonyl compounds on aqueous atmospheric particles is a primary motivation of the present study. Here, we have shown that it is possible to generate accurate hydration extent predictions for a number of the most atmospherically abundant carbonyl compounds (Tables 2 and 3),[7] as well as a number of important SOA components that are thought to derive from isoprene photochemistry and SOA processing (Table 3).[39−41] Atmospheric processing of organic compounds tends to add electronegative oxygen-containing functional groups. Our model suggests that these new multifunctional carbonyl compounds are more likely to be hydrated under atmospheric conditions than simple aldehydes and ketones. More specifically, our results support those of previous studies, which have shown that glyoxal[13−15] and methylglyoxal[16,17] undergo significant hydration under atmospheric conditions. Interestingly, experimental measurements illustrate that the terminal carbonyl group of methylglyoxal undergoes hydration, followed by hydration of the internal carbonyl group, but that a compound with a hydrated internal carbonyl group and an unhydrated terminal carbonyl group was not observed.[31] This result indicates that either our prediction that K_H for the internal carbonyl group of methylglyoxal is also greater than unity is incorrect or that kinetic effects prohibit the experimental observation of this species on the experimental time scales.

The predictions of this model suggest that some of the carbonyl organosulfates detected in SOA in Atlanta, GA,[41] such as 1-sulfatoacetone ion and 2-sulfato acetaldehyde ion are present in their hydrated form, while other organosulfates, such as 4-sulfato-2-butanone, will not be significantly hydrated under atmospheric conditions. Our predictions also suggest that the aldehydic isoprene oxidation intermediates, IEPOXO,[39,42] will undergo significant hydration on aqueous atmospheric particles, which would lead to greater partitioning to the particle phase, which in turn would allow for more efficient processing by nucleophilic reactions involving IEPOXO's epoxide functional group. However, if the epoxide group of IEPOX is hydrolyzed first, the hydration of the carbonyl group is predicted to be less favorable, which indicates that epoxide functional groups act to increase the hydration propensity of carbonyl groups even more than hydroxyl groups. The high-NO_x isoprene oxidation product nitratoacetone[43] is also predicted to be significantly hydrated, which would also increase its partitioning to the particle phase and potentially promote such processes as the hydrolysis of the nitrate group and/or substitution of the nitrate group by sulfate.[44,45]

This model has shown that many atmospherically important carbonyl compounds are predicted to undergo significant hydration on aqueous atmospheric particles, which confers lower volatility and higher Henry's law solubility on the hydrated compound as compared to the unhydrated compounds, which has important ramifications for gas-particle partitioning and subsequent particle phase reactivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.0c00322.

Computational MG2MS, van't Hoff-adjusted, and experimental thermodynamic parameters (PDF)

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Notes

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