

# Secondary Organic Aerosol Formation by Heterogeneous Reactions of Aldehydes and Ketones: A Quantum Mechanical Study

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Experimental studies have provided convincing evidence that aerosol-phase heterogeneous chemical reactions (possibly acid-catalyzed) are involved to some extent in the formation of secondary organic aerosol (SOA). We present a stepwise procedure to determine physical properties such as heats of formation, standard entropies, Gibbs free energies of formation, and solvation energies from quantum mechanics (QM), for various short-chain aldehydes and ketones. We show that quantum mechanical gas-phase Gibbs free energies of formation compare reasonably well with the literature values with a root-mean-square (RMS) value of 1.83 kcal/mol for the selected compounds. These QM results are then used to determine the equilibrium constants (reported as  $\log K$ ) of aerosol-phase chemical reactions, including hydration reactions and aldol condensation for formaldehyde, acetaldehyde, acetone, butanal, hexanal, and glyoxal. Results are in qualitative agreement with previous studies. In addition, the QM results for glyoxal reactions are consistent with experimental observations. To our knowledge, this is the first QM study that supports observations of atmospheric particle-phase reactions. Despite the significant uncertainties in the absolute values from the QM calculations, the results are potentially useful in determining the relative thermodynamic tendency for atmospheric aerosol-phase reactions.

## Introduction

Secondary organic aerosol (SOA) formation by gas/particle (G/P) partitioning has traditionally focused on low volatility products. The quantity of SOA formed can be estimated using absorptive or adsorptive G/P partitioning theory which assumes that this quantity is governed strongly by the vapor pressure of the compound as well as the liquid-phase activity coefficient (1–5). Recent experimental work has suggested that the amount of SOA formed in a number of systems exceeds that based purely on G/P partitioning of low vapor pressure oxidation product (6–10). Evidence also indicates that relatively volatile oxidation products, especially alde-

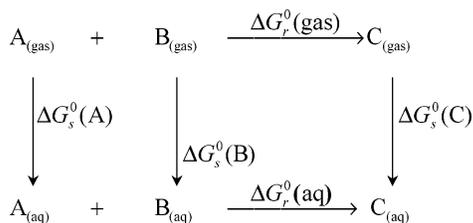
hydes and ketones, are being absorbed into the aerosol phase where they undergo aerosol-phase chemical reactions. The reaction products have relatively low vapor pressures compared to their parent compounds, which lead to additional partitioning from gas to particle phase and, hence, increase the organic particulate material (OPM). Aerosol-phase reactions, such as hydration, polymerization, hemiacetal/acetal formation, and aldol condensation, have been postulated as a means by which low volatility compounds can be formed thereby increasing the amount of OPM formed beyond that due to G/P partitioning of low vapor pressure gas-phase oxidation products alone.

Theoretical studies by Barsanti and Pankow (11) have shown, however, that reactions such as hydration, polymerization, and hemiacetal/acetal formation are not thermodynamically favorable under atmospheric conditions. Their results do suggest that aldol condensation may be thermodynamically favorable. These results seem to deviate from experimental observation (9). On the other hand, they have shown that diol and subsequent oligomer formation are favorable for glyoxal (12), and these findings are consistent with experiments (13–15). While the experimental studies have provided convincing evidence that aerosol-phase chemical reactions (possibly acid-catalyzed) are involved to some extent in formation of SOA, uncertainty remains as to the likely aerosol-phase chemical reactions involving absorbed gas-phase organic compounds.

The reactive uptake mechanism for relatively small, volatile organic compounds (short-chain aldehydes and ketones) is not well understood. Hydration is invariably the first step for volatile organics to dissolve into the particle phase, followed by various (possibly acid-catalyzed) reactions such as polymerization, hemiacetal/acetal formation, and aldol condensation. As suggested by Barsanti and Pankow (11), aldol condensation may be the most accessible reaction path for additional OPM formation.

In the current study, we investigate the thermodynamic feasibility of various particle-phase heterogeneous reactions for some common atmospheric carbonyl compounds using quantum mechanical methods. In particular, we consider the hydration reaction and aldol condensation for small, short-chain aldehydes and ketones, such as formaldehyde, acetaldehyde, acetone, butanal, and hexanal. We also include glyoxal in our investigation. The relatively simple structure of glyoxal as well as its clear importance as an atmospheric oxidation product of a number of hydrocarbons makes it an excellent candidate for theoretical study. Recent studies (13–16) have shown aerosol growth by heterogeneous reactions of gas-phase glyoxal. The thermodynamic feasibility of a proposed glyoxal reaction pathway (14) is evaluated in our study. Similar to the studies by Barsanti and Pankow (11, 12), the thermodynamic analysis presented in this work is independent of the actual reaction pathway. The goal is to present a method to identify potential particle-phase reactions that may contribute to atmospheric OPM, and the extent of OPM contribution if the reactions are kinetically favorable. This study does not yield any information regarding the kinetics; therefore, evidence of additional OPM formation may remain unobservable at short time scales. On the other hand, we focus only on determining the solution-phase equilibrium constant,  $K$ , which is the governing factor of the overall tendency of the reactions in the particle. Owing to the chemical complexity of atmospheric aerosols, one is often faced with the difficulty in obtaining physical properties for species for which limited experimental data exist. Here we apply novel quantum chemistry methods as an alternative

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**FIGURE 1. Thermodynamic cycle for computation of energy changes of reaction in the gas phase and solution. Adapted from ref 38.**

predictive approach, which may reduce the number of parameters or experimental data required.

### Computational Method

To calculate equilibrium constants ( $K$ ) of the reactions, the standard Gibbs free energy of a reaction ( $\Delta G_r^0$ ) are needed and can be calculated by the standard Gibbs free energy of formation ( $\Delta G_f^0$ ). It is also related to the equilibrium constant ( $K$ ) according to the fundamental equation

$$\Delta G_r^0 = \sum_j \nu_j \Delta G_{f,j}^0 = -RT \ln K \quad (1)$$

where  $\nu_j$  is the stoichiometric coefficient for  $j$  in the reaction, and  $\Delta G_{f,j}^0$  is the standard Gibbs free energy of formation for  $j$ .  $\Delta G_{f,j}^0$  can be determined using gas-phase heats of formations and standard entropies ( $\Delta G_{f,j}^0 = \Delta H_{f,j}^0 - T\Delta S_j^0$ ). Then, as illustrated by Figure 1, the free energy of reaction in aqueous solution,  $\Delta G_r^0(\text{aq})$ , is related to the gas-phase free energy of reaction,  $\Delta G_r^0(\text{gas})$  by adding the solvation energies of the species,  $\Delta G_s^0$ .

$$\Delta G_r^0(\text{aq}) = \Delta G_r^0(\text{gas}, 1\text{M}) + \sum_j \nu_j \Delta G_s^0 \quad (2)$$

All the necessary quantities ( $\Delta H_{f,j}^0$ ,  $\Delta S_j^0$ , and  $\Delta G_s^0$ ) can be determined by QM, and the procedure will be described below. It should be noted here that proper standard state conditions should be used for the free energy calculations in eq 2. The standard state for gas-phase reactions is 1 atm at 298 K, while the standard state for aqueous solution is 1 M at 298 K. A brief description of the standard state conversion (38) is provided in the Supporting Information.

**Gas-Phase Standard Heats of Formation.** QM calculated standard heats of formation would be the first step to obtain free energies of formation for eq 1. QM heats of formation at 298 K is given by the equation

$$\Delta H_{f,j}^0(\text{QM}) = E_{\text{elec}} + E_{\text{zpe}} + \Delta H_{(0-298\text{K})} + \Delta H_{298\text{K}}^* \quad (3)$$

To obtain the ground-state energy ( $E_{\text{elec}}$ ), the molecules were optimized using DFT/X3LYP, with a fairly large basis set aug-cc-pVTZ(-f) (17) in the gas phase. For molecules with different conformations, geometry optimization using a smaller basic set 6-31g\*\* (18) was carried out to select 4 (or 5) relatively stable conformations. Further optimizations were then performed for the selected structures at the higher level to calculate  $E_{\text{elec}}$ . The vibrational frequency calculations are performed for the most stable structure at the HF/631g\*\* level in the gas phase with a scaling factor 0.8992. This scaling factor was determined by comparing the theoretical harmonic vibrational frequencies with the corresponding experimental values utilizing a total of 122 molecules (1066 individual vibrations) and a least-squares approach (19). The frequency calculations ascertain the structure of the molecules and provide zero point vibrational energy ( $E_{\text{zpe}}$ ), the thermal vibrational, rotational, and translational enthalpy from 0 to 298 K ( $\Delta H_{(0-298\text{K})}$ ). The last term in eq 3,  $\Delta H_{298\text{K}}^*$ , allows for

corrections between the theoretical heats of formation, referenced to the electrons and nuclei separated an infinite distance, and experimental values, referenced to the elements at standard temperature and pressures. A common reference is the enthalpies of formation for the neutral atoms in the gas phase, so

$$\Delta H_{298\text{K}}^* = \sum_{i=1}^n n_i (h_i^0 - h_i^{\text{QM}}) \quad (4)$$

where  $n$  is the number of elements in the compound, and  $n_i$  is the number of atoms of each element.  $h_i^0$  is the experimental atomic heats of formation in the gas phase (20), and  $h_i^{\text{QM}}$  is the theoretical value

$$h_i^{\text{QM}} = E_i^{\text{elec}} + \frac{3}{2}RT - PV = E_i^{\text{elec}} + \frac{1}{2}RT \quad (5)$$

where  $E_i^{\text{elec}}$  is the quantum electronic energy,  $3/2 RT$  is the translational energy at 298 K and the ideal gas law is applied for  $PV$ ,  $R$  is the gas constant, and  $T$  is the temperature.

Large discrepancies can be found between the QM calculated heats of formation using eq 3–5 and the experimental heats of formation. Improvement can be made by applying the correction scheme such as the J2 model of Dunitz et al. (21) to the enthalpies. The J2 model is based on the generalized valence bond-localized Møller–Plesset method (GVB-LMP2), and it uses a three-parameter correction term composed of  $\sigma$  bond and  $\pi$  bond parameters and an additional parameter to account for the difference of lone pairs between the molecule and the separated atoms. Recently, Blanco and Goddard (22) developed a correction scheme closely following the J2 corrections (21), but their “chemical bond” scheme for high level corrections (CBHLC) applies to DFT quantum calculations and only consists of the two  $\sigma$  bond and  $\pi$  bond parameters. Details of the CBHLC scheme are given in the Supporting Information.

All calculations were performed using the Jaguar 6.0 package (23). QM calculations were carried out using DFT with X3LYP. X3LYP is an extended hybrid density functional that has been shown to be an accurate and practical theoretical method (24–26), with a particularly accurate estimation of van der Waals interactions.

**Standard Free Energies of Formation and Equilibrium Constants.** Adding the entropy term to the QM gas-phase heats of formation will give us the standard Gibbs free energy,  $\Delta G_r^0$ , at 298 K

$$\Delta G_{f,j}^0 = \Delta H_{f,j}^0(\text{QM}) - T(S_{j,298\text{K}}(\text{QM}) - \sum_{i=1}^n n_i S_{i,298\text{K}}) \quad (6)$$

where  $S_{j,298\text{K}}(\text{QM})$  is the entropy of the compound at 298 K, and  $S_{i,298\text{K}}$  is the entropy for the elements in their reference states (20). At this point, we can obtain the gas-phase Gibbs free energies of reaction using eq 1. To obtain solution-phase energies, the solvation effect is accounted by the free energy of solvation, ( $\Delta G_s^0$ ), as shown in Figure 1.

**Solution-Phase Energy.** QM determined solvation energies,  $\Delta G_s^0$ , for both the parent compounds and reaction products are shown in Table 2. Solvation energy ( $\Delta G_s^0$ ) describes the interaction of a solute with a surrounding solvent. Change in entropies due to conformational changes of the molecules from gas phase to aqueous phase is minimized by reoptimization of the compounds at X3LYP/cc-pVTZ(-f) using the implicit continuum solvent model (27–29). In a continuum model, solute atoms are treated explicitly, and the solvent is represented as a continuum dielectric medium. The electrostatic contribution to the solvation free energy is computed using the Poisson–Boltzmann (PB)

**TABLE 1. Quantum Calculated Free Energies of Formation<sup>a</sup>**

	$\Delta G_f^0(\text{exp})^b$	$\Delta G_f^0(\text{Joback}) (30)$	$\delta G^d$	$\Delta G_f^0(\text{QM})$	$\delta G^e$
water	-54.60 ± 0.11	c		-53.92	0.68
formaldehyde	-24.51 ± 0.74	c		-24.96	-0.45
acetaldehyde	-31.84 ± 0.96	-31.90	-0.06	-33.68	-1.84
acetone	-36.14 ± 1.08	-36.91	-0.77	-39.29	-3.16
butanal	-27.78 ± 0.83	-27.88	-0.10	-29.06	-1.28
hexanal	-23.90 ± 0.72	-23.86	0.04	-23.72	0.18
glyoxal	-45.31	-55.67	-10.36	-45.23	0.07
ethylene glycol	-72.08 ± 2.16	-73.49	-1.40	-69.41	2.67
hydroxyacetone	-68.07 ± 6.81	-69.59	-1.52	-70.04	-1.97
2,4-pentanedione	-64.37 ± 0.64	-63.68	0.69	-61.77	2.60
glutaraldehyde	-48.58 ± 2.43	-49.64	-1.06	-46.61	1.97
cyclopropane carboxylic acid	-58.49 ± 1.75	-71.74	-13.25	-56.80	1.69

<sup>a</sup> The literature free energies of formation and group contribution (Joback) method estimated values are included for comparison. Absolute errors ( $\delta G$ ) are also shown. All values are in kcal/mol. <sup>b</sup> Gas-phase literature values and uncertainties of free energies of formation,  $\Delta G_f^0(\text{exp})$  are obtained from DIPPR database (31). <sup>c</sup> The group contribution Joback method (30) lacks sufficient groups to estimate  $\Delta G_f^0$  for water and formaldehyde. <sup>d</sup>  $\delta G = \Delta G_f^0(\text{Joback}) - \Delta G_f^0(\text{exp})$ . <sup>e</sup>  $\delta G = \Delta G_f^0(\text{QM}) - \Delta G_f^0(\text{exp})$ .

**TABLE 2. Quantum Calculated Free Energies of Formation,  $\Delta G_f^0$ , and Solvation Energies,  $\Delta G_s^0$ , at the X3LYP/cc-pvtz(-f) Level<sup>a</sup>**

	$\Delta G_f^0(\text{QM})$ (kcal/mol)	$\Delta G_s^0(\text{QM})$ (kcal/mol)	$\Delta G_s^0(\text{exp})^a$ (kcal/mol)
<b>Parent Compounds</b>			
water	-53.92	-7.47	-10.5
formaldehyde	-24.96	-2.89	
acetaldehyde	-33.68	-4.17	-3.50
glyoxal	-45.23	-4.02	
acetone	-39.29	-4.97	-3.80
butanal	-29.06	-3.52	-3.18
hexanal	-23.72	-3.17	-2.81
<b>Hydrates of</b>			
formaldehyde	-78.90	-8.94	
acetaldehyde	-82.19	-12.06	
acetone	-77.48	-10.90	
butanal	-77.13	-7.34	
hexanal	-71.54	-6.23	
<b><math>\beta</math>-Hydroxycarbonyls of</b>			
acetaldehyde	-58.17	-10.64	
acetone	-66.69	-7.78	
butanal	-45.54	-9.03	
hexanal	-30.61	-7.78	
<b><math>\alpha,\beta</math>-Unsaturated Carbonyls of</b>			
acetaldehyde	-12.90	-5.42	
acetone	-14.89	-4.63	
butanal	-4.19	-3.88	
hexanal	9.18	-3.06	

<sup>a</sup> Experimental solvation energies are obtained from ref 37, except for water (20).

method (see the Supporting Information). The PB equation is valid under conditions where dissolved electrolytes are present in the solvent, but the current implementation of the QM solvation model is confined to zero ionic strength. The effect on the equilibrium constant for reactions in solution with dissolved electrolytes remains unknown because the change in solvation effect due to ionic strength of the solvent varies with species. Although the solvation model is limited to solution zero ionic strength, we can apply the solvation model to any solvent with the proper choice of dielectric constant. Water is chosen in this study because it is often the most important component in aerosols.

## Results and Discussion

Calculated QM free energies of formation in the gas phase,  $\Delta G_f^0(\text{QM})$ , and estimated free energies of formation were

**TABLE 3. Quantum Calculated Enthalpies and Gibbs Free Energies of Reactions for Hydration and Aldol Condensation at  $T = 298 \text{ K}^a$** 

	$\Delta H_r(\text{gas})$	$\Delta G_r(\text{gas})$	$\Delta G_r(\text{aq})$
<b>Hydration: Aldehyde + H<sub>2</sub>O = Hydrate</b>			
formaldehyde	-10.81	-0.03	-0.50
acetaldehyde	-6.31	5.41	3.11
acetone	4.00	15.73	15.37
butanal	-5.55	5.85	7.61
hexanal	-5.73	6.09	8.61
<b>Aldol Condensation: 2 Carbonyls = <math>\alpha,\beta</math>-Unsaturated Carbonyls + Water</b>			
acetaldehyde	-1.09	0.54	-4.00
acetone	8.24	9.78	7.61
butanal	-3.22	0.01	-4.30
hexanal	0.86	2.70	-1.50

<sup>a</sup> All energies are in kcal/mol.

obtained from the group contribution "Joback method" (30),  $\Delta G_f^0(\text{Joback})$ . Both estimations are compared to the gas-phase literature values (31), and the differences ( $\delta G$ ) are calculated (see Table 1). Group contribution methods are widely used because of their efficiency and accuracy. Barsanti and Pankow (11) found that the estimated  $\Delta G_f^0$  by the Joback method agrees with the values from Yaws (32) to  $\pm 0.7$  kcal/mol ( $\pm 3$  kJ/mol) for a set of compounds including alcohols, aldehydes, and ketones. However, as for all predictive methods, group contribution methods are limited by the experimental data that were used in the parametrization, which may be problematic for multifunctional compounds where experimental data are scarce. For the selected 12 compounds, the root-mean-square (RMS) value for errors between  $\Delta G_f^0(\text{Joback})$  and  $\Delta G_f^0(\text{exp})$  is 5.80 kcal/mol (vs 0.90 kcal/mol if we exclude glyoxal and cyclopropane carboxylic acid). Since the CBHLC corrections is extended to include multifunctional oxygenates, the RMS value for the discrepancies between QM  $\Delta G_f^0(\text{gas})$  and  $\Delta G_f^0(\text{exp})$  is 1.83 kcal/mol for all compounds shown in Table 1. Although the RMS deviation for QM  $\Delta G_f^0(\text{gas})$  is significantly higher (1.90 kcal/mol vs 0.90 for Joback method when glyoxal and cyclopropane carboxylic acid are excluded), the predictive power of QM methods can be of great use for species that have not been studied experimentally.

Gibbs free energies of reaction for hydration reaction and aldol condensation are calculated (Table 3) for both gas and aqueous phases. Enthalpies of reaction,  $\Delta H_r(\text{gas})$ , are included for reference. Hydration and aldol condensation are more favorable for aldehydes (formaldehyde, acetaldehyde, butanal, and hexanal) than for acetone, shown by the

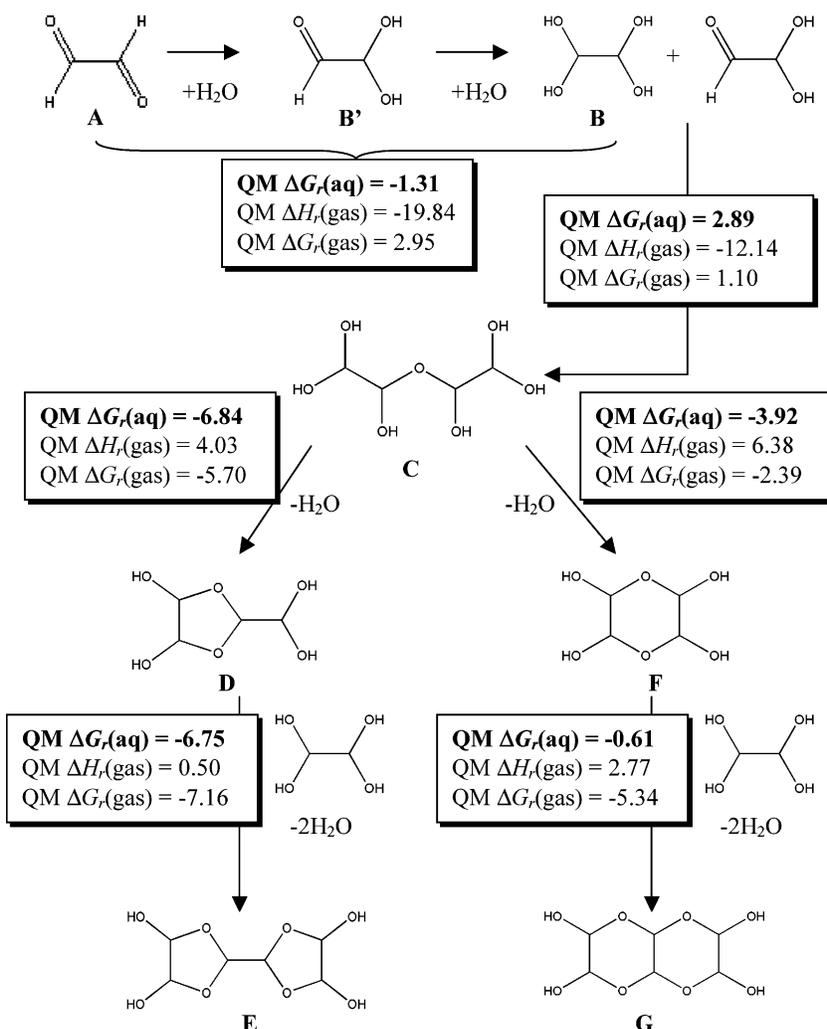


FIGURE 2. A summary of the suggested reaction pathway for glyoxal in particular matter by Liggio et. al. (14). Quantum calculations were done for the proposed structures in the scheme. QM calculated enthalpies and free energies of reactions were shown. All values are in kcal/mol.

TABLE 4. Quantum Calculated  $\log K$  in the Gas Phase and Solution, Estimated  $\log K$  in Liquid Solution, and Experimental  $\log K$  for Hydration Reaction and Aldol Condensation at  $P = 1$  atm and  $T = 298$  K<sup>a</sup>

	QM log $K$ (gas)	QM log $K$ (aq)	ref 11 log $K$ (liq)	exptl log $K$ (aq)
<b>Hydration: Aldehyde + H<sub>2</sub>O = Hydrate</b>				
formaldehyde	0.02	0.36	0.62	
acetaldehyde	-3.96	-2.28	-6.46	-1.67 <sup>a</sup>
acetone	-11.53	-11.26	-13.72	
butanal	-4.29	-5.58	-6.55	
hexanal	-4.47	-6.31	-7.07	
<b>Aldol Condensation: 2 Carbonyls = <math>\alpha,\beta</math>-Unsaturated Carbonyls + Water</b>				
acetaldehyde	-0.40	2.93	2.22	
acetone	-7.17	-5.58	-1.79	
butanal	-0.01	3.15	4.14	
hexanal	-1.98	1.10	3.34	

<sup>a</sup> Calculated from the value of ref 33, divided by 55.6 M.

calculated  $\Delta H_r$  and  $\Delta G_r$ . Equilibrium constants (reported as  $\log K$ ) are calculated and shown in Table 4. Estimated  $\log K$  values in liquid solution,  $\log K$  (liq), where it is assumed that the solution are mostly organic, from Barsanti and Pankow (11) were also included for reference. The quantum calculated  $\log K$  values in aqueous solution,  $\log K$  (aq), follow the same trend as the estimated  $\log K$  (liq) for both hydration reaction and aldol condensation. Results show that the

hydration reactions for the most simple aldehydes and ketones (acetone) are unfavorable (Table 3). The  $-0.50$  kcal/mol of free energy of hydration for formaldehyde are too small to be considered significant. Kroll et. al. (13) have shown that most simple carbonyls (such as formaldehyde and octanal) do not contribute additional OPM via heterogeneous reactions, except glyoxal. Our results seem to support their findings even though the two sets of compounds are mostly different. Experimental thermodynamic data for hydration and aldol condensation of aldehydes and ketones are rare. A study by Tur'yan (33) concluded that the average hydration constant,  $K_h$ , for acetaldehyde in bulk solution is  $1.19 \pm 0.05$  ( $\log K_h$  (aq) =  $-1.67$ ). Our QM  $\log K_h$  (aq) =  $-2.28$ , showing that the QM result significantly underestimates the extent of hydration for acetaldehyde.

**Uncertainties.** QM predicted free energies of reaction,  $\Delta G_r^0$ (aq), and equilibrium constants ( $\log K$ ) remain questionable because of the QM calculated entropies. For "flexible" molecules with low frequency vibrations (such as hexanal), the QM harmonic oscillator approximation is inadequate and leads to large errors in gas-phase entropies. Additional errors can be caused by neglecting the intermolecular contributions that may be present in the condensed phase. Other issues can arise from multiple conformations of the reactants/products. While a full conformational search is computationally expensive, we have taken a considerable

**TABLE 5. Quantum Calculated Enthalpies ( $\Delta H_f^0$ ) and Free Energies ( $\Delta G_f^0$ ) of Formation and Solvation Energies ( $\Delta G_s^0$ )<sup>a</sup>**

compound	$\Delta H_f^0$ (QM) (kcal/mol)	$\Delta G_f^0$ (QM) (kcal/mol)	$\Delta G_s^0$ (QM) (kcal/mol)
A	-50.65	-45.23	-4.14
B'	-117.63	-98.36	-10.56
B	-184.66	-150.12	-15.34
C	-314.42	-247.39	-21.92
D	-253.31	-199.17	-18.63
E	-323.30	-248.61	-27.26
F	-250.96	-195.86	-18.26
G	-318.68	-243.48	-22.08

<sup>a</sup> The structures for compound labeled A–G are shown in Figure 2.

effort in locating the minimum energy conformation. Yet, it is still possible that we have not located the minimum.

An estimation of the uncertainty for the QM predicted  $\Delta G_f^0$ (aq) is provided instead of error approximation for individual reaction because of the lack of experimental data. The RMS error in heats of formation using the CBHLC method is found to be 2.11 kcal/mol for a set of 50 organic compounds. The RMS error in entropies is estimated to be 1.39 kcal/mol for the 12 compounds in this study, and the RMS error of the solvation energies is found to be 0.9 kcal/mol from the original reference of the implicit continuum solvent model (27). With these numbers, the uncertainty in  $\Delta G_f^0$ (aq) for a reaction such as aldol condensation is estimated to be as large as 5.4 kcal/mol.

**Glyoxal.** The reaction mechanism for glyoxal heterogeneous reactions in particular matter suggested by Liggio et al. (14) is based on generic hydration and acetal formation. A summary of the reaction pathway is given in Figure 2; the whole process was written acid-catalyzed and was supported by the particle mass spectra in their study. They also suggested that mechanism C to E in Figure 2 is more favorable than C to G, agreeing with earlier studies (34–36).

Later studies (13, 16) also observed significant aerosol growth with glyoxal and supported the findings by Liggio et al. (14, 15). Kröll et al. (13) supported the mass spectra data by Liggio et al. (14, 15) in both masses and intensities, and they both have and suggested that additional pathways are necessary to account for the large glyoxal uptake in the particle phase (13, 15). Hastings et al. (16) found the threshold humidity and particle growth rate are consistent with Liggio et al. (14) at a glyoxal concentration 4 orders of magnitude difference. The consistency suggests that the gem-diol compound B is highly favored, and the surface water on the particle becomes saturated; glyoxal polymerization may therefore proceed at the highest rates. The unique ability of glyoxal to partition into surface water at high concentration may explain observations by Kröll et al. (13) where additional aerosol growth was only observed for glyoxal.

Gibbs free energies of reaction,  $\Delta G_r$ , for the glyoxal reactions in both gas and aqueous phases could be obtained using the computational methods described; enthalpies of reactions are included for reference (Table 5). As illustrated in Figure 2, the free energies of reaction in solution,  $\Delta G_r$ (aq), have indicated that hydration is favorable. The results are qualitatively consistency with experimental observations, but the number is small and is within the uncertainty estimated (~5 kcal/mol). We expect the effect of not including solute–solvent interactions in the condensed phase would be the greatest contributor, as compound B contains 4 hydroxyl groups that may interact with water. The formation of intermediate C is positive, but the subsequent steps in the cyclic acetal formation are favorable enough to compensate. Acetal formation is overall favorable and consistent with

experiments. Our results suggest that cyclic acetal formation may proceed with an intermediate other than C. Again, the positive  $\Delta G_r$ (aq) for B to C are within the uncertainty, so the positive  $\Delta G_r$ (aq) can be just an artifact caused by the limitations of our QM methods. Our  $\Delta G_r$ (aq) results, however, have clearly shown that mechanism C to E is preferred over mechanism C to G, if C can be a valid intermediate compound. To conclude, our quantum calculated results are in qualitative agreement with experimental observations for glyoxal reactions.

All in all, estimation of free energies using quantum methods remains a difficult problem, and the results are quantitatively unreliable. Nevertheless, in the evaluation of thermodynamic tendency of various reactions, where the emphasis is not on the absolute but relative changes in free energies, quantum methods can still serve as useful tools for first approximation, especially for species with no available data. Despite the limitations of the quantum calculations, we have shown that QM results are consistent with experimental observations.

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### Supporting Information Available

Computational details and results of QM calculated heats of formation and estimated absolute entropies and additional information about the CBHLC correction scheme, standard state conversion, and solvation energy model are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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