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Can a Single Water Molecule Really Catalyze the Acetaldehyde + OH Reaction in Tropospheric Conditions?

Cristina Iuga,[†,‡] J. Raul Alvarez-Idaboy,*[,†] Lino Reyes,[§] and Annik Vivier-Bunge[†]

[†]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, México DF 09340, México, [‡]Facultad de Química, Departamento de Física y Química Teórica, Universidad Nacional Autónoma de México, México DF 04510, México, and [§]Facultad de Química, Departamento de Química Orgánica, Universidad Nacional Autónoma de México, México DF 04510, México

ABSTRACT In recent publications there has been considerable speculation about the possible role of a single water molecule in the catalysis of reactions between organic volatile compounds and OH radicals. In this work we reanalyze the effect of water in the acetaldehyde + OH reaction, using quantum chemistry and computational kinetics calculations in a pseudosecond order mechanism, at average atmospheric water concentrations and temperatures. We show that one water molecule definitely *does not* accelerate the acetaldehyde + OH reaction under atmospheric conditions. The apparent rate coefficient is considerably smaller than the one in the absence of water, regardless of the method of calculation. According to present results, the possible role of water molecules has been overestimated and new experiments are needed.

SECTION Atmospheric, Environmental and Green Chemistry
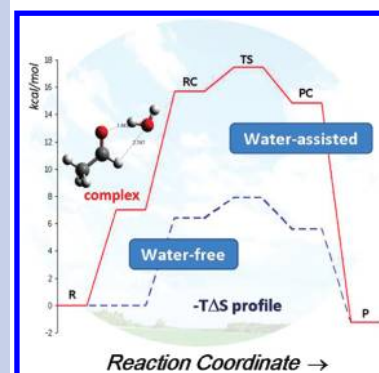
A recent publication in *Science*[1] has suggested the possible role of a single water molecule in the oxidation reaction of acetaldehyde by a hydroxyl radical.[1] The authors used a wind-tunnel apparatus with detector lasers to demonstrate that water accelerated the reaction between gaseous hydroxide radicals and acetaldehyde molecules (OH + CH₃CHO → H₂O + CH₃O), especially at low temperatures. Accompanying theoretical calculations showed that one water molecule forms hydrogen-bonds with an acetaldehyde molecule, making it more vulnerable to OH radical attack. A comment by Smith in the Perspectives Section in the same issue of *Science*[2] acknowledged the interest of Vöhringer-Martinez's work, but questioned its relevance to atmospheric chemistry. In fact, the kinetic effect of the presence of water had already been studied in 2004 by Canneaux et al.[3] in a theoretical study of the reaction of acetone with OH radicals. Their conclusion was that the tropospheric concentration of OH−acetone−water complexes would be very small, but that they probably could be detected experimentally. Since then, several articles have been published involving possible one-molecule catalysis in reactions of OH radicals with other organic volatile compounds.[4,5] There has also been considerable speculation about the role of water complexes and other hydrogen-bonded molecular complexes on the kinetics and dynamics of gas-phase free radical reactions.[6,7]

In recent work we have shown[8] that, in the case of bimolecular processes that yield a single product (A+B→C), it is not always possible to extrapolate results obtained in chamber experiments to processes at atmospheric concentrations. Under these pseudo-first-order conditions, the relative equilibrium concentrations depend strongly on the concentration of the excess reactant.

Since the simultaneous collision of three molecules is very improbable, for an A+B+C reaction the termolecular mechanism is ruled out. Hence, the most probable mechanism consists of two consecutive bimolecular elementary steps, possibly followed by unimolecular steps.

For the particular case of a hydrogen abstraction reaction between an oxygenated volatile organic compound (VOC) and an OH radical, the gas phase reaction is known to be a two-step reaction involving the reversible formation of a prereactive complex.[9] Analogously, it seems reasonable to assume that the water-assisted reaction mechanism consists of three steps: the first one is the reversible formation of a complex between water and one of the reactants; in the second step, the termolecular complex is formed reversibly; the third step is the irreversible unimolecular hydrogen abstraction. In principle, this would be a third-order rate constant reaction, not directly comparable with the water-free second-order reaction. However, the concentration of atmospheric water, although variable, is always in large excess with respect to both the OH and the aldehyde concentration. This, together with the fact that water regenerates, allows us to use fixed water concentrations to obtain pseudo-second-order rate constants that depend parametrically on water concentration. The additional advantage of this approach is that it shows, within the accuracy of the calculations, which water concentration is critical in order to observe catalysis.
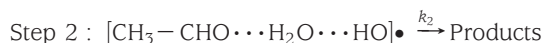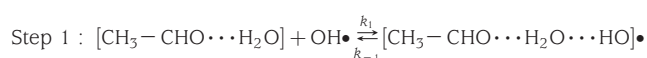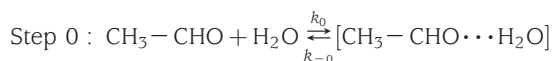
In this work we reanalyze the effect of water in the acetaldehyde + OH reaction, using quantum chemistry and computational kinetics calculations in a pseudo-second-order mechanism, at average atmospheric water concentrations and temperatures. The emphasis is placed on the pseudo-second-order kinetic calculations, since they yield an unambiguous answer to the question of the possible catalytic effect of a single water molecule in atmospheric conditions.

Electronic structure calculations are performed with the Gaussian 03 program using two standard quantum chemistry methods. Unrestricted calculations are used for open shell systems. Frequency calculations are performed for all the stationary points at the same level of theory as the geometry optimization, and local minima and transition states are identified by the number of imaginary frequencies.

The rate coefficients (k) are computed using conventional transition state theory (TST)[10−12] as implemented in The-Rate program[13] at the Computational Science and Engineering Online Website (www.cseo.net).[14] Tunneling corrections are taken into account, assuming unsymmetrical Eckart barriers. The energy values, partition functions, and thermodynamic data are taken from the quantum-mechanical calculations.

For the reaction in the presence of one water molecule, the pseudo-second-order rate constant is calculated using a typical water concentration (5×10^{17} molecule/cm^3). This methodology has been successfully used previously in theoretical work on water−VOC complexes and OH−water complexes.[15,16] It is the main difference between this work and the one in ref 1.

The following steps in the acetaldehyde + OH reaction in the presence of water have been considered:

$$\text{Step 0}: \ CH_3-CHO + H_2O \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} [CH_3-CHO\cdots H_2O]$$

$$\text{Step 1}: \ [CH_3-CHO\cdots H_2O] + OH\bullet \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [CH_3-CHO\cdots H_2O\cdots HO]\bullet$$

$$\text{Step 2}: \ [CH_3-CHO\cdots H_2O\cdots HO]\bullet \overset{k_2}{\rightarrow} \text{Products}$$

In Step 0, complexation between a water molecule and acetaldehyde is assumed to be more important than either water−OH or acetaldehyde−OH, due to the very small concentration of OH radicals. In fact, the OH−water complex concentration has been calculated to be 5.5×10^4 clusters/cm^3.[16]

Complex formation is a process that occurs with a large entropy loss and therefore the decrease of enthalpy barriers by H_2O does not necessarily lead to an enhancement of the rate of the reaction. Thus, in order to gain correct insight into the effect of water on the reaction of OH with acetaldehyde, we report standard Gibbs free energies for all stationary-point structures.

No experimental data are available for the amount of acetaldehyde−water complex formed under tropospheric conditions, but it can be estimated theoretically using the following expression:

$$[\text{complex}] = K_C[CH_3CHO][H_2O] \tag{1}$$

where K_C is calculated from quantum chemistry results and [CH$_3$CHO][H$_2$O] is obtained using average concentrations for acetaldehyde and water vapor.

First, in order to test the validity of the theoretical method employed, we tried several quantum chemistry methods to reproduce the existent experimental data for the concentration of water dimer in water vapor at room temperature, using a water concentration that corresponds to a relative humidity of 100 % at 298.15 K. The results are 1.45×10^{15} and 7.82×10^{14} at the CCSD(T)/6-311++G(d,p)//MP2(FC)/6-311++G-(d,p) and CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G-(d,p) levels, respectively, in very good agreement with the experimental results of Pfeilsticker et al. (6×10^{14} molecules cm^{-3} [17]) and with previous calculations performed with different accurate methods.[18] Thus, in this work we have calculated the equilibrium constant for Step 0 of the acetaldehyde + OH reaction using the partition functions of the acetaldehyde−H$_2$O complex and those of the separated reactants obtained with both methods. The results are given as Supporting Information in Table S1, for temperatures between 140 and 340 K. K_C values range between 10^{-19} at 140 K and 10^{-23} molecules^{-1} cm^3 at 340 K. At room temperature K_C is of the order of 10^{-22} molecules^{-1} cm^3.

Then, using eq 1 and considering that the acetaldehyde concentration is about 1 ppm (2.46×10^{13} molecules/cm^3) and the water concentration in the troposphere is about 7.95×10^{17} molecules cm^{-3}, it is clear that, at tropospheric temperatures, the complex concentration is necessarily very small, which means that very little acetaldehyde is complexed with water under tropospheric conditions. Of course this result depends on the actual concentrations of water and of acetaldehyde. In Table S2 of the Supporting Information, the complex concentration is shown in terms of those of water and acetaldehyde at 298 K. It can be seen that, even at the largest water and acetaldehyde concentrations, it is always several orders of magnitude smaller than the amount of free acetaldehyde, and consequently the complex represents only about 0.01 % of the total acetaldehyde. In fact, these results are not really surprising. It is well-known that water−water interactions are much stronger than acetaldehyde−water interactions[3] and yet only about 1 % of the total water molecules form dimers at 298 K and tropospheric concentrations.

The importance of Step 0 cannot be overemphasized for the reaction in tropospheric conditions. Ignoring Step 0 is equivalent to assuming that all the acetaldehyde is complexed with water, which is absolutely not true. At very low temperatures, however, K_C may be as much as 3 orders of magnitude larger than at room temperatures, and most of the acetaldehyde could then be in the form of the complex, in agreement with Vöhringer-Martinez et al. results.[1]

A summary of energy and free energy results obtained with both methods for the stationary points along the reaction path is shown in Table S3 of the Supporting Information.

The energy and free energy profiles are shown in Figure 1 for the reaction with and without water. It is important to point out that, in the gas phase reaction, the energy and free energy barriers, $\Delta E^\ddagger$ and $\Delta G^\ddagger$ are obtained as the difference between the energies of the transition state and those of the preactive
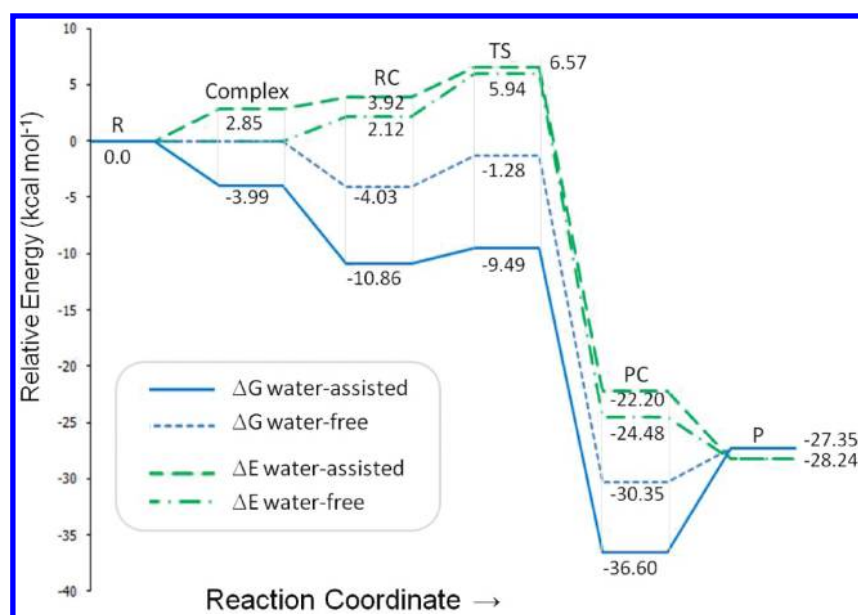
Figure 1. Relative energy and Gibbs free energy profiles in the water-assisted and water-free acetaldehyde + OH reactions at the CCSD(T)//BH&HLYP level (R = Reactants, RC = prereactive complex, TS = transition state, PC = product complex, P = products).

Table 1. Calculated Equilibrium Constants (in molecules^{-1} cm^3), Rate Constants k^{eff} (in cm^3 molecule^{-1} s^{-1}) and Tunneling Corrections (κ) at 298 K, in the Water-Free and Water-Assisted Acetaldehyde + OH Reactions

	K_{eq0}	K_{eq1}	κ	k_2	k^{eff}
		Water-free: $k^{\mathrm{eff}} = \sigma K_{\mathrm{eq1}} k_2 \kappa$			
CCSD(T)//MP2(FC)		7.93×10^{-22}	2.70	4.39×10^{10}	9.61×10^{-11}
CCSD(T)//BHandHLYP		1.14×10^{-21}	1.40	9.87×10^{9}	1.58×10^{-11}
		Water assisted: $k^{\mathrm{eff}} = \sigma K_{\mathrm{eq0}} K_{\mathrm{eq1}} k_2 \kappa$ [water]			
CCSD(T)//MP2(FC)	1.16×10^{-22}	5.50×10^{-21}	2.97	3.67×10^{10}	5.13×10^{-14}
CCSD(T)//BHandHLYP	1.65×10^{-22}	6.81×10^{-21}	2.78	6.99×10^{10}	1.61×10^{-13}

complex, while in the water-assisted reaction, $\Delta E^{\ddagger}$ and $\Delta G^{\ddagger}$ are the energies at the transition state minus the ones of the OH−H$_2$O−CH$_3$CHO termolecular complex.

Thus, if Step 0 is ignored and the rate constant is calculated as

$$k^{\mathrm{eff}} = \sigma K_{\mathrm{eq1}} k_2 \kappa \qquad (2)$$

(where κ is the tunnelling correction and σ is the reaction path degeneracy) the reaction rate is indeed faster in the presence of water, and the catalyzed reaction seems to be more favorable than in the gas phase.. In fact, MP2 calculations, which were used in ref 1, present the largest difference in free energy between the water-assisted and the water-free reactions. However, if Step 0 is taken into account, there is a negligible amount of water-−acetaldehyde complex to begin with, and thus it is the water-free gas-phase path that determines the rate of the reaction. Then, the correct expression to calculate the effective rate constant is

$$k^{\mathrm{eff}} = \sigma K_{\mathrm{eq0}} K_{\mathrm{eq1}} k_2 \kappa [\mathrm{water}] \qquad (3)$$

The water-free and water-assisted rate constants at 298 K are shown in Table 1 for the two methods employed. We have used a water concentration of 7.38×10^{17} molecules cm^{-3}, which corresponds to a 3 % atmospheric water concentration.

The variation with temperature has also been analyzed, and results are given in Table 2 for the 200−340 K temperature range and a fixed 3 % water concentration. Slight changes are noticeable only below 220 K, which constitutes an impossible condition, since a 3 % water concentration in the gas phase is not possible at temperatures significantly below 298.15 K. For more details, the water-assisted rate constants calculated for different water concentrations and in the same temperature range are given in Table S4 (Supporting Information).

As in any quantum chemical modeling, it is important to comment about our confidence in the calculated Gibbs free energies. The methodology used here has been tested in our group for dozens of chemical reactions, and excellent agreement with experimental results has been obtained. Additionally, our complexation free energies are in excellent agreement with the few available experimental data as well as with previous calculations.[15−18]

In conclusion, it is safe to state that one water molecule definitely *does not* accelerate the acetaldehyde + OH reaction under atmospheric conditions. The apparent rate coefficient taking into account atmospheric water concentration is considerably smaller than the one in the absence of water,

Table 2. Calculated Rate Constants (in cm^3 molecule^{-1} s^{-1}) between 200 and 340 K in the Water-Free and Water-Assisted Acetaldehyde + OH Reactions

	200	220	240	260	280	300	320	340
Water-free $k^{eff} = \sigma K_{eq1} k_2 \kappa$								
CCSD(T)//MP2(FC)	7.04×10^{-10}	3.81×10^{-10}	2.36×10^{-10}	1.61×10^{-10}	1.18×10^{-10}	9.19×10^{-11}	7.48×10^{-11}	6.31×10^{-11}
CCSD(T)//BHandHLYP	4.61×10^{-11}	3.32×10^{-11}	2.57×10^{-11}	2.09×10^{-11}	1.78×10^{-11}	1.56×10^{-11}	1.41×10^{-11}	1.29×10^{-11}
Water-assisted $k^{eff} = \sigma K_{eq0} K_{eq1} k_2 \kappa_2$ [water]								
CCSD(T)//MP2(FC)	1.55×10^{-10}	1.60×10^{-11}	2.48×10^{-12}	5.23×10^{-13}	1.41×10^{-13}	4.63×10^{-14}	1.78×10^{-14}	7.75×10^{-15}
CCSD(T)//BHandHLYP	8.61×10^{-10}	7.57×10^{-11}	1.03×10^{-11}	1.94×10^{-12}	4.77×10^{-13}	1.44×10^{-13}	5.16×10^{-14}	2.12×10^{-14}

independent of the method of calculation. The apparent disagreement between the present results and the experimentally observed rate coefficients in ref 1 could be due to a possible catalytic effect of associations of water molecules, or else could be because the experimental conditions do not match the ones in an atmospheric environment. The conclusions in this work show that the role of a single water molecule has been overestimated, and new experiments are needed.

SUPPORTING INFORMATION AVAILABLE Calculated equilibrium constant K_C of the water−acetaldehyde complex at different temperatures. Acetaldehyde−water complex concentration as a function of acetaldehyde and water concentrations. Relative energies in the acetaldehyde + OH reaction. Calculated rate constants between 200 and 340 K, in the acetaldehyde + OH reaction for different water concentrations. Entropy profiles for the reaction in the water-free gas phase and in the presence of one water molecule. Cartesian coordinates and termochemistry data for all the stationary structures optimized at BHandHLYP/6-311++g** and MP2(FC)/6-311++g** levels. This material is available free of charge via Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: jidaboy@unam.mx.

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