Effect of Water Vapor on the Combination and Disproportionation of Ethyl Radicals in the Gas Phase

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The role of H_2O vapor on the disproportionation/combination ratio (k_d/k_c) of C_2H_5 radical reactions in the gas phase has been investigated experimentally and compared to that observed previously in aqueous solution. At added water pressures of 20 kPa (15 Torr), the k_d/k_c ratio remains unchanged from that observed in its absence. The relationship of the invariant ratio to bonding and solvation phenomena are discussed.

The disproportionation and combination reactions of the thermalized ethyl radical (C_2H_5) have been extensively investigated over the years and several reviews written about this system.[1,2] The disproportionation/combination ratio ($k_d/k_c = k_1/k_2$), in the gas phase, for which there is wide agreement,[1,2] is equal to 0.14 ± 0.01

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad (1)$$

$$\rightarrow n\text{-}C_4H_{10} \qquad (2)$$

The role of water has been shown to be significant, at least in solution, where measurements suggest that the k_d/k_c ratio is quite dependent upon the solvent and its polarity. The experimental values range from the gas-phase value of 0.14, in the case of nonpolar solvents, up to 0.35 when the solvent is water.[3] An unequivocal and agreed upon rationale for the large difference is not available but specific polar solvation of the radicals involved in the reactions[2,3] seems to have an impact on the reaction products.

Reactions 1 and 2 are reasonably fast in the gas-phase, of the order of 1 effective collision per 10 or a rate constant[4,5] of $k_1 + k_2 = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Under "ordinary" laboratory experimental conditions involving laser flash photolysis of an appropriate precursor, radical concentrations are usually[6] of the order of 10^{14} cm^{-3}. Consider the addition of 2 kPa (15 Torr = 5.3×10^{17} cm^{-3}) of H_2O to the gas-phase system containing the ethyl radical. The canonical ethyl radical in such a system will have about 5×10^3 more collisions with a H_2O molecule than with another C_2H_5 radical based simply upon concentration considerations and neglecting the mass difference. Furthermore, because the rate constant of $k_1 + k_2$ is about 1/10 collisions, an ethyl will collide with a water molecule about 5×10^4 times before an effective reaction occurs with yet another ethyl species. However, if the ethyl/water collision is likewise ineffective, then the addition of 93.3 kPa (700 Torr) of He might provide a mechanism for removal of any excess energy produced in the photolysis.

The nature of transition state(s) for the radical−radical disproportionation and combination reactions has been a subject of continuing interest. As noted in the review of Gibian and Corley,[1] it was thought that both disproportionation and combination channels occurred through a common excited dimer transition state. The adduct could either be quenched to give the combination product or rearrange and dissociate to the disproportionation products. However, studies involving partially deuterated ethyl radicals[7] reinforce the opposing view that the combination is a head-to-head interaction between two radicals while disproportionation occurs analogous to hydrogen abstraction through a head-to-tail process. However, the A factor for disproportionation reactions are generally significantly larger than those for abstraction reactions.

Determination of the k_d/k_c ratio in the presence and absence of water can provide significant insight on the question: What might be the attraction between a highly polar water and the radical−radical reaction adduct(s) and/or the free electron on the ethyl radical which is the reactive site of the combination reaction?[1] If the interaction is significant in the gas phase, one might expect to observe a change in the k_d/k_c ratio if the mechanisms for combination and disproportionation are different and the reactive position for the combination reaction might be "taken" by a species that has a water molecule associated with the electron.

There are neither experimental measurements nor theoretical predictions for the interaction of a hydrocarbon free radical, such as the ethyl radical, with H_2O. The hydrogen-bonding interaction between the OH radical and water, however, has been investigated theoretically.[8] The $^2A''$ state of the ($OH{\cdot}H_2O$) system, at all levels of theory, is predicted to be a minimum in the potential energy surface with a D_0 equal to about 14.5 kJ mol^{-1} which is comparable to that of the water dimer itself. In comparison, whereas the unpaired electron on the radical provides something of an anionic flavor, electrons are not usually considered to be anions and their bonding toward water is significantly stronger than for a radical. Attractive potentials of several anions toward water have been determined. For example, the bond strength of the $O^-{\cdots}H_2O$ system is >105 kJ mol^{-1} [9], and a D_0 for the $O^-(H_2O)$ system has been calculated

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to be equal to 106.36 kJ mol^{-1}.[10] The interaction is relatively long range as the O−H bond that interacts with the O^- anion is longer than the free O−H bond itself.[10] Even larger systems have binding energies that are similar to the above, e.g., the binding energy of carboxylates $(RCO_2)^-$ to H_2O is about 84 kJ mol^{-1}.[11]

The goal of this experiment was to determine the effect of water vapor, in the gas phase, upon the ratio of reactions 1 and 2 and thereby obtain some information upon the nature of the attraction between the polar water molecule and the ethyl radical and/or adduct of the radical−radical reaction.

Photolysis of diethyl ketone (DEK) is a convenient source of ethyl radicals and has been used in this study. Following photolysis of DEK/He mixtures at 248 nm, the distribution of products was measured using GC-MS and the k_d/k_c ratio was determined and was found to be in excellent agreement with the literature value of 0.14. The partial pressure of DEK was kept identical and the total pressure (mainly He) varied between 2 and 93.3 kPa (15 and 700 Torr). No effect upon the k_d/k_c ratio vs pressure was observed. To examine the effect of water vapor, similar photolytic precursor concentrations were used along with added 2 kPa (15 Torr) of H_2O vapor (essentially the vapor pressure of H_2O at 298 K). No additional He was added in the 20 kPa (15 Torr) experiments. A ratio of $k_d/k_c = 0.17 \pm 0.03$ was determined in the presence of 2 kPa of H_2O which is, within the uncertainties of measurements, in agreement with the k_d/k_c value (0.14 ± 0.03) when only He is present in the mixture. For measurements at high pressure, He was added to the DEK/H_2O mixture (with a maximum H_2O vapor pressure of 2.0 kPa) to increase the total system pressure to 93.3 kPa (700 Torr). As before, the product distributions following photolysis were obtained via GC-MS product analysis. The k_d/k_c ratio, 0.11 ± 0.03, determined at the high pressure of 93.3 kPa and in the presence of water, is slightly lower than the corresponding k_d/k_c value at 2.0 kPa (0.17 ± 0.03), but considering the measurement uncertainties, it appears there is no appreciable effect of water vapor on the k_d/k_c ratio at either high or low pressures.

In certain processes such as the reaction of SO_3 with H_2O, the role of water dimers appears to be important.[12] An evaluation of the equilibrium population of water dimers under some particular experimental conditions is suggested to be ill-posed[13] but earlier work, based upon thermal conductivity measurements, suggested a dimer concentration of 0.01 at saturation at 373 K.[14] Higher *n*-mers are even less significant, and based upon mass, the *n*-mer collision rate with some particular species present in the system under investigation will be less than that of the monomer or dimer.

Of great import we find that since there is no variation of the gas-phase k_d/k_c ratio in the presence of water vapor the simple picture of a polar water molecule attaching to the active site of the ethyl radical and, thereby, affecting the product ratio is not viable. Also these results indicate that it is likely that the product adduct(s) leading to the combination and disproportionation products are not significantly different with regard to interaction with the polar water molecules or perhaps they are identical. In aqueous solution, the number of water molecules in the first solvation shell of both anions and neutrals is about 4−5.[15,16] Presumably, in the gas-phase, the total solvation of a transient species, such as the C_2H_5 radical, does not occur during the temporal history of the species. In comparison, solvation in solutions occurs in the time frame of hundreds of fs.[17,18] An accurate computational and experimental determination of the temporal profile of the $C_2H_5(H_2O)$ complex would be elucidating. Also, these results indicate that the presence of polar water molecules does not affect the transition state(s) for the combination and disproportionation channels. Detailed theoretical and additional experimental studies of the important interactions of water in reactive media are sorely needed to better understand the complex radical−water and/or adduct−water interactions.

TABLE 1: k_d/k_c at Total Pressures of 2 kPa (15 Torr) and 93.3 kPa (700 Torr), without and with the Presence of 2 kPa (15 Torr) of H_2O Vapor[a]

photolyzed mixture	P = 2 kPa	P = 93.3 kPa
DEK/He	0.14 ± 0.03	0.13 ± 0.03
DEK/H_2O/He	0.17 ± 0.03	0.11 ± 0.02

[a] The partial pressure of DEK is 30 Pa (0.22 Torr) to 70 Pa (0.5 Torr)

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