

# Hydration and Alcohol-Addition Reactions of Gas-Phase Lithium-Alcohol Complexes

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## 1. Introduction

Complexes composed of metal ions and organic ligands have been observed to undergo association reactions with small molecules in the gas-phase. Wu and Brodbelt have demonstrated that Cu(I) and Ag(I) complexes (with pyridyl and bipyridyl ligands) will form water adducts in an ion trap<sup>1</sup>. Hanna and Van Stipdonk showed similar behavior for Ag (I) alcohol complexes<sup>2</sup>.

Motivating our efforts is the idea that detailed information about intrinsic hydration reaction kinetics and thermodynamics will benefit the development of artificial enzymes that use metal centers to activate water. In this study we investigated the effect of single alcohol ligands and changing the ligand on Li<sup>+</sup> complexes. Li<sup>+</sup> is a model group I metal that is being used to develop analytical approaches to be applied to systems incorporating Cu<sup>2+</sup> and Zn<sup>2+</sup>.

## 2. Methods

Mass spectrometry experiments were conducted on a Finnigan LCQ-Deca electrospray ionization, ion-trap mass spectrometer (Complex ions were generated from spray solutions containing Li<sup>+</sup> and alcohol.) The CID parameters were the following: He collision gas, activation amplitudes of ~20-30% (of 5V), q<sub>z</sub> values of 0.3-0.35 and activation time of 1 to 1000 msec. In this study, Li<sup>+</sup> alcohol complexes (alcohols used were ethanol, propanol, isopropanol, n-butanol and 2-butanol) (ROH + Li)<sup>+</sup> were isolated and stored in an ion trap mass spectrometer for periods ranging from 1 to 1000 msec. During the isolation period, the complexes reacted with gas-phase water at a pressure of ~10<sup>-6</sup> torr.

## 3. Results and Discussion

Mass spectra resulting from the isolation and storage of the (ROH + Li)<sup>+</sup> complexes are shown in figure 1. For each case the isolation time was 600 msec. The spectra in figure 1 shows the precursor complex (ROH + Li)<sup>+</sup> and the hydrated complex (ROH + Li + H<sub>2</sub>O)<sup>+</sup>

The reaction schemes and associated rate constants are shown in equations 1,2,3 and table 1 below. To obtain the rate constants, fractional abundances of reactant and product ions were calculated by dividing the relative intensities of the precursor ion and adduct ions by the total ion abundances. The changes in fractional abundances with time were used to obtain relative values of rate constants for the addition reactions using Chemical Kinetic Simulator™ Program. Rate constants for the reactions in the model system were changed constantly until the concentration curves generated by the model fit the observed changes in the fractional abundances.

Results from the spectra and rate constants suggest that the rate of hydration reaction increases with the increase in the length of the hydrocarbon group of the alcohol and for a given alcohol (propanol or butanol) with the degree of branching. Hence the reactivity of n-propanol is comparable to 2-butanol. This is attributed to increasing polarizability with chain length and partial delocalization of the charge

The reactions were conducted under pseudo first order conditions since the concentration of H<sub>2</sub>O was in excess and as such the rate constants calculated included this conditions.

Isolation time : 600 msec

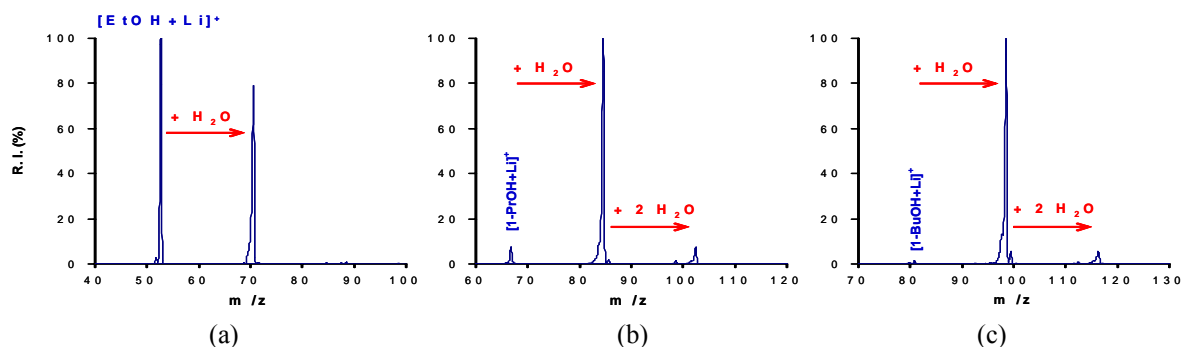
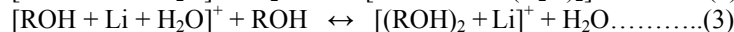
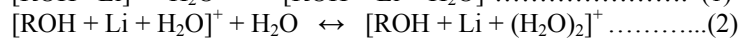
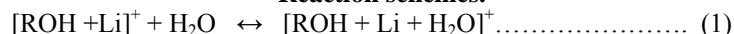


Fig 1. Mass spectra generated by isolation and storage of  $\text{Li}^+$  complexes. (a) EtOH, (b) n-PrOH and (c) n-ButOH. The isolation time for each spectrum was 600msec.

	$k_1$	$k_{-1}$	$k_2$	$k_{-2}$	$k_3$	$k_{-3}$
Ethanol	8e-11	3e-04	1e-11	6e-04	2e-11	7e-04
1-propanol	3.1e-10	1.1e-04	1.7e-11	9e-04	4e-11	5.5e-09
2-propanol	2.6e-10	1.5e-04	1.4e-11	9e-04	4.5e-11	5.4e-09
1-butanol	7e-10	4.8e-05	2.5e-11	1.7e-03	1.5e-11	5e-04
2-butanol	5.5e-10	5e-05	2e-11	2e-03	2.3e-11	5e-04

Table 1: Relative rate constants obtained through kinetic modeling of temporal changes in ion abundances.  $k_1, k_2, k_3$  and  $k_{-1}, k_{-2}, k_{-3}$  are forward and reverse reactions respectively.

#### Reaction schemes.



#### 4. Conclusion

In this study, we measured the intrinsic hydration rates for  $[\text{ROH} + \text{Li}]^+$  complexes (ROH= ethanol, n-propanol, isopropanol, n-butanol and 2-butanol). In the gas-phase reactions the above complex was able to co-ordinate a maximum of two ligands; water or alcohol. This is due to the bulky group causing steric hindrance. From the results it is observed that the extent of electron delocalization is dependent upon the length of the alkyl group.

#### 5. Acknowledgements

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