Potassium-containing hypermetalated compounds and their water complexes: K_3OH , $K_4(OH)_2$, $K_2(OH)(H_2O)$, and $K_3(OH)(H_2O)$

R.-C. Jiang

Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

and

T.-M. Su

*Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC
and The Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, ROC*

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Potassium-containing hypermetalated compounds, K_3OH and $K_4(OH)_2$, and their water complexes, $K_2(OH)(H_2O)$ and $K_3(OH)(H_2O)$, were generated in a flow reactor and studied by photoionization mass spectrometry. The photoionization threshold energies of K_3OH , $K_3(OH)(H_2O)$, $K_4(OH)_2$, and $K_2(OH)(H_2O)$, were measured to be 3.78, 3.97, 3.54, and 3.69 (± 0.08) eV, respectively. The enthalpies of the water-complex formation were determined to be -16.7 ± 3.3 and -14.0 ± 2.8 kcal/mol for $K_2(OH)(H_2O)$ and $K_3(OH)(H_2O)$, respectively.

1. Introduction

Hypermetalated molecules of alkali metals, especially the lithium compounds, have recently attracted considerable attention [1–8]. Theoretical molecular orbital calculations were mainly focused on the nature of the chemical bonding of these species [1–4]. The experimental work concentrated on the generation and study of the mass-selected photoionization spectra of these species [5–8]. Until now, only a limited number of these compounds have been studied either theoretically and/or experimentally. For the class of hypermetalated compounds of alkali metals containing a hydroxyl group, there is only one theoretical work on Na_2OH , and Na_3OH [3] and a recent experimental work on K_2OH [8]. In this communication, we report the generation and detection of a series of potassium-containing hypermetalated compounds involving hydroxyl groups and their water complexes. These compounds include K_3OH , $K_4(OH)_2$, $K_2(OH)(H_2O)$, and

$K_3(OH)(H_2O)$. Their appearance ionization potentials and the enthalpies of the formation of the water complexes are also determined. Although these complexes are stable in the isolated form, they can be regarded as the reaction intermediates during the reaction between the potassium metal and water molecules. Photoionization studies of these molecular complexes in the gas phase will shed some light on the nature and the stability of this type of bonding. The method of the generation of these species also suggests the opportunities for further experimental studies.

2. Experimental method and results

The experimental apparatus consisted of a photoionization mass spectrometer coupled with a flow reactor. The details have been described previously [8]. For the present report, we briefly describe the experimental conditions: Potassium vapor generated

by a potassium oven and carried by an Ar flow is cooled down to around the ambient temperature by mixing with a gas mixture of Ar and H₂O vapor. The flow reactor was thermally regulated and the temperature was monitored by thermocouples. The total gas pressure of the flow reactor was kept at around 2.5 Torr. The flow reactor was then sampled by a 1 mm orifice and then collimated by a skimmer. The vacuum chambers were differentially pumped. The molecular beam was photoionized by a high-pressure Hg lamp. The ions were detected by a quadrupole mass spectrometer. The molecular beam, the lamp radiation and the quadrupole mass filter were spatially perpendicular to each other.

After the introduction of water vapor, a layer of solid KOH was formed around the outlet of the tube of the potassium vapor flow. In generating the potassium-containing hypermetalated molecules involving the hydroxyl group, the quantity of the water vapor introduced into the flow reactor is rather crucial. If a comparatively excess amount of water vapor was introduced, essentially no photoionization mass signals could be detected at 307 nm radiation. On reduction of the water vapor pressure to around 0.25 Torr, the dominant photoionization mass peaks become K₂ and KH₂O. On further reduction of the water vapor pressure to about 0.08 Torr, K₂OH·(H₂O), K₃OH, and K₃(OH)(H₂O) start to dominate the spectrum. Some minor peaks, such as KH₂O, K₂OH(H₂O)₂ (131 amu), and K₃(OH)₂(H₂O)₃ (205 amu), are also present. A typical photoionization mass spectrum under these experimental conditions is shown in fig. 1a. On still further reduction of the water vapor pressure to 0.005 Torr, all the water-containing complexes, such as K₂(OH)(H₂O), K₃(OH)(H₂O), essentially disappear. The pure hypermetalated hydroxides K₂OH, K₃OH, and K₄(OH)₂ become dominant in the spectrum. A typical spectrum is shown in fig. 1b. At this point, if one completely turns off the water vapor, these mass peaks gradually decay away. All the signals disappear if one turns off the potassium vapor.

The generation of K₂OH, K₃OH, K₃(OH)₂, K₄(OH)₂, and other minor related species, is due to the chemical reactions between the hot potassium vapor and the solid KOH formed around the outlet of the flow tube:

where $n=2, 3, 4$, and $m=1, 2$ with $m < n$.

The generation of the water-containing complexes is due to the recombination reactions of the hypermetalated compounds with the water vapor in the gas phase in the flow reactor:

where $n=2, 3, 4$; $m=1, 2$, with $m < n$; and $p=1, 2$, with $p \leq n$. M represents any third body present in the flow.

Fig. 2 shows the photoionization efficiencies of the four main species: K₃OH, K₄(OH)₂, K₂(OH)(H₂O), and K₃(OH)(H₂O). The main spectral features are due to the line spectra of the high-pressure 1 kW Hg lamp. The smooth curves are the best-fitting simulations around the ionization threshold region by assuming the photoionization efficiency of these complexes to be the pseudo-Watanabe type function [8]. The monochromator slit function of the spectrometer and the spectral intensity of the light source were also taken into account in these simulations. The appearance ionization potentials are determined to be 3.78, 3.97, 3.54, and 3.69 (± 0.08) eV for K₃OH, K₃(OH)(H₂O), K₄(OH)₂, and K₂(OH)(H₂O), respectively.

The enthalpies of formation of the water complexes are determined by the van 't Hoff plots of the equilibrium constants expressed by $K = \alpha I_{wc} / I_p p_w$. Here I_{wc} and I_p are the photoionization signals of the water complexes and their parent molecules, respectively, α is a temperature-independent proportional constant, and p_w is the water pressure. If we assume that under low-resolution photon radiation, the photoionization efficiencies are constants when the photon frequency is above but not far away from the threshold energy [9], it follows that the photoionization signal would be directly proportional to the concentration of the complexes. The good agreement between the simulation and the experimental curves in fig. 2 also supports this assumption. In this way, we obtained the enthalpies of formation of the water complexes of K₂OH·H₂O to be -16.7 ± 3.3 kcal/mol and of K₃OH·H₂O to be -14.0 ± 2.8 kcal/mol. The

Fig. 1. Photoionization mass spectrum of potassium-containing hypermetalated molecules and their water complexes at 0.08 Torr (a) and 0.005 Torr (b) of water vapor pressure in the flow reactor. The photon wavelength was set at 307 nm.

20% error is mainly due to the uncertainty in the flow temperature.

3. Discussion

The photoionization potential of K_3OH is higher than that of K_2OH (3.55 eV). This is consistent with

Fig. 2. Photoionization efficiency spectra of potassium-containing hypermetalated molecules and their water complexes. The smooth curves are the theoretical simulations with the pseudo-Watanabe type photoionization efficiency.

the accepted rule of compound clusters which states that clusters containing an even number of valence electrons are more stable [7]. Despite the even number of the valence electrons in $K_4(OH)_2$, its pho-

toionization potential is close to that of K_2OH . One could regard the formation of $K_4(OH)_2$ as the addition of a KOH electric-dipole molecule to a K_3OH molecule. Apparently, the pairing orientation is such

that all the potassium atoms are clustered together to form hypermetallic bonding [3]. The increase of the energy due to the buildup of the positive charge in the metal cluster compensates the stabilization energy gained by the pairing of the two valence electrons. In the present measurements, the photoionization potentials of the water complexes are consistently higher than those of their parent compounds. If one assumes that the appearance ionization potential is close to the adiabatic ionization potential, and starts from the hydration enthalpies of $K_2(OH)$ and $K_3(OH)$, one finds the hydration enthalpies of $K_2^+(OH)$ and $K_3^+(OH)$ to be -13.5 and $-9.6 (\pm 5)$ kcal/mol, respectively. Contrary to common belief, these values are less than the hydration energies of the corresponding neutral species. The most likely reason is that the equilibrium configurations of the neutral and ionic species of the water complexes are appreciably different from each other so that the vertical ionization energies are no longer close to the adiabatic ionization potentials.

According to molecular orbital calculations [3], the alkali-containing hypermetalated hydroxides can be regarded as ionic molecules formed by a negatively charged hydroxyl group and a positively charged metal cluster. The interaction between an ionic molecule and a polar solvent molecule, such as water or ammonia molecules, is rather strong. This information is important in understanding the solvation process and the dynamics of electrolyte solutions. Although matrix-isolation technique could yield the vibrational spectra of these species and the interaction strength could be inferred from the shift of the vibrational frequencies, the bonding energies were not available in these measurements. The pres-

ent enthalpy measurements of the first hydration of these ionic species gave us the first direct experimental information of the interaction strength.

The present observation of the potassium-containing hypermetalated compounds and their water complexes around room temperature demonstrates the stability and structural richness these species may demonstrate in the gas phase. The other alkali-metal atoms, especially the lighter ones, are expected to behave similarly because of their similarity in the hypermetallic bonding [3].

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