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LETTERS

Dehydrogenation Reaction from a Dihydrogen Bonded Precursor Complex in the Gas Phase

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In this paper, we present mass spectroscopic evidence for the dehydrogenation reaction from a dihydrogen bonded complex between phenol and borane-trimethylamine following resonance enhanced multiphoton ionization in the gas phase. The evidence presented herein is based on observed fragmentation pattern of the complex cation having high internal energy. To the best of our knowledge, it is the first report of such observation.

I. Introduction

Hydrogen bonding has profound impact on structure and reactivity, both in chemistry and biology. In the past decade, a new type of interaction, analogous to hydrogen bonding between two oppositely charged hydrogen atoms, termed "dihydrogen bonding", was identified in crystals of transition metal complexes and borane-amine adducts.[1] The dihydrogen bond can be represented as E−H···H−X, where E and X are electropositive and electronegative elements, respectively, with respect to hydrogen. Recently, we demonstrated the formation of dihydrogen bonded complexes of phenol with borane-dimethylamine[2] (BDMA) and borane-trimethylamine[3] (BTMA) in the gas phase.

An important upshot of dihydrogen bond is the elimination of molecular hydrogen leading to dehydrogenation reaction. This reaction is thermodynamically favorable due to large free energy for the formation of H_2. Liu and Hoffmann[4] investigated the dihydrogen bonded LiH···HF complex, which, however, was not stable owing to large exothermicity of the reaction $LiH + HF \rightarrow LiF + H_2$. Atwood et al.[5] have reported the structure of 2,2,6,6-tetramethylpiperidine-alane complex containing dihydrogen bond, which, further, readily undergoes loss of molecular hydrogen. In this case, the dihydrogen bond can be viewed as an intermediate for the dehydrogenation reaction. Later, an ab initio study by Kulkarni[6] on many main-group model compounds has revealed that the dihydrogen bond is indeed a transition state on the reaction coordinate of dehydrogenation reaction.

In this letter, we report the mass spectrometric evidence for the dehydrogenation reaction in the gas phase, following resonance enhanced multiphoton ionization (REMPI) of the dihydrogen bonded phenol-BTMA complex in supersonic free jet. Because spectroscopy and structure of the parent complex is intimately related to the dehydrogenation reaction, we first review the spectroscopy and structure of phenol-BTMA complex prior to the presentation of the dehydrogenation reaction.

II. Experiment

Details of the experimental set up for recording the laser induced fluorescence (LIF) excitation spectrum, fluorescence detected infrared (FDIR), and IR−UV hole-burning spectra are reported elsewhere.[3,7] For recording the mass spectra and mass resolved excitation spectra, cations generated following REMPI were repelled into a quadrupole mass filter (Extranuclear 4−270−9) with a field strength of about 15 V/cm and were detected using a channel electron multiplier (Murata, Ceratron).[8] The mass spectra were recorded both in low and high-resolution modes. In high-resolution mode, the quadrupole mass filter was

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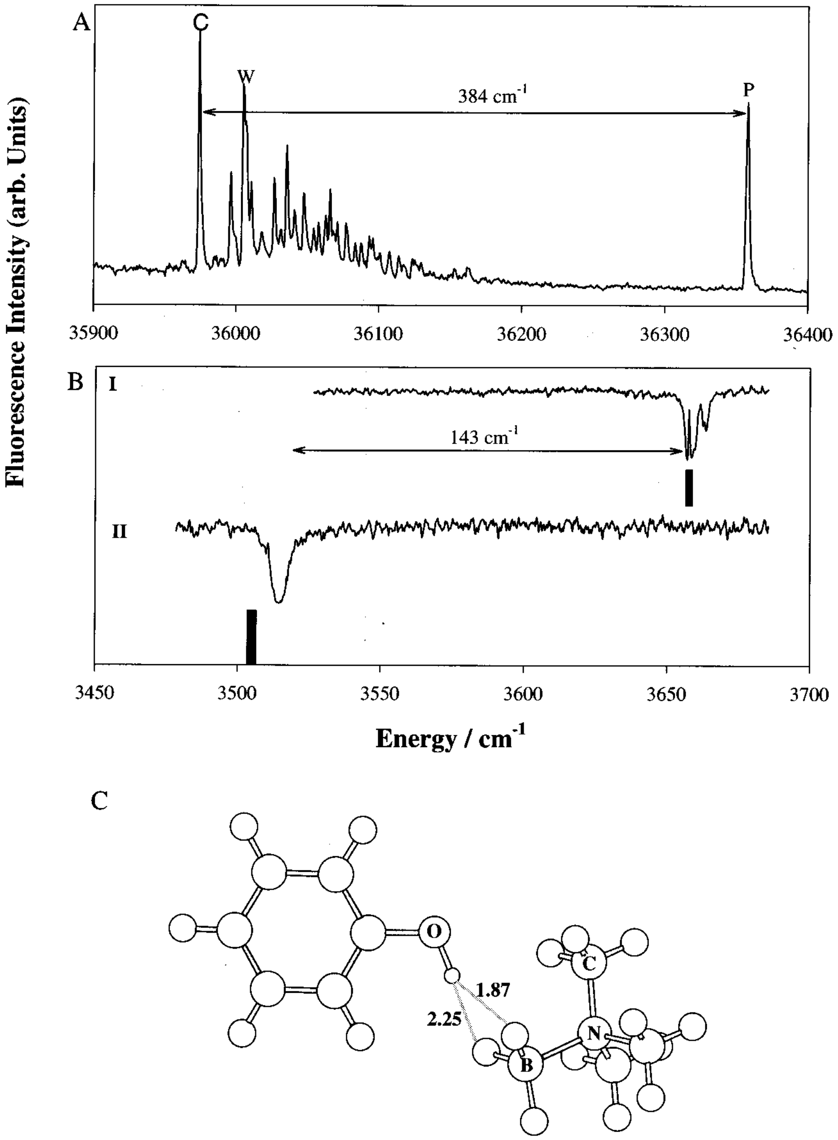


Figure 1. (A) LIF excitation spectrum of phenol and its cluster with BTMA. Peaks marked with C, W, and P are the origin transitions of phenol-BTMA, phenol-H_2O, and bare phenol, respectively. (B) FDIR spectrum of bare phenol (Trace I) and phenol-BTMA (Trace II). Also shown are the calculated vibrational frequencies. (C) Calculated structure of phenol-BTMA complex. Distances are in angstroms and the labels B, C, N, and O correspond to boron, carbon, nitrogen and oxygen atoms, respectively.

calibrated using mass signals of benzene, benzene dimer, phenol, and known mass fragments of phenol. Resolution of the mass filter ($M/\Delta M$) was found to be about 150 at mass 58. Binary clusters of phenol with BTMA were generated in a supersonic free jet by passing helium buffer gas at 4 atm over phenol (Aldrich; vacuum sublimated) kept at room temperature and mixing with BTMA (Kanto Chemicals) in a sample compartment heated to 315 K. The mixture was expanded supersonically through a 0.8 mm pulsed nozzle.

III. Results & Discussion

Figure 1A shows LIF excitation spectrum of phenol in the presence of BTMA. Several new transitions appear after addition of BTMA to sample compartment, of which, the lowest energy transition at 35964 cm^{-1} marked “C” is the band origin transition of phenol-BTMA complex. This transition is 384 cm^{-1} red shifted from the corresponding band of bare phenol. Figure 1B shows the FDIR spectrum of bare phenol (Trace I) and of the phenol-BTMA complex (Trace II). A single vibrational transition at 3657 cm^{-1} was observed in the case of bare phenol, corresponding to O−H stretching, which is in good agreement with that reported elsewhere.[9] The observed splitting is due to ambient water vapor absorption, which modulates the IR laser intensity. FDIR spectrum of the phenol-BTMA complex (Trace II) shows a relatively broad band at 3514 cm^{-1}, corresponding to O−H stretching vibration, which is shifted to a lower frequency by 143 cm^{-1} from that of bare phenol. The spectral shifts in both electronic and O−H vibrational transitions are in good correlation with each other when compared with other hydrogen bonded clusters of phenol, such as phenol-H_2O and phenol-MeOH, and indicate formation of hydrogen bonding between phenolic O−H and BTMA. IR−UV hole burning spectroscopy (not presented here, see ref 3) clearly demonstrated the presence of only one isomer of phenol-BTMA in present experimental conditions. Several new transitions, which appeared in the LIF excitation spectrum, were therefore assigned as vibronic bands associated with the band origin transition of the complex. Consistent with the experimental observations, we found only one stable minimum for the phenol-BTMA complex at B3LYP/6-31++G (*d*, *p*) level of calculations using GAUSS-

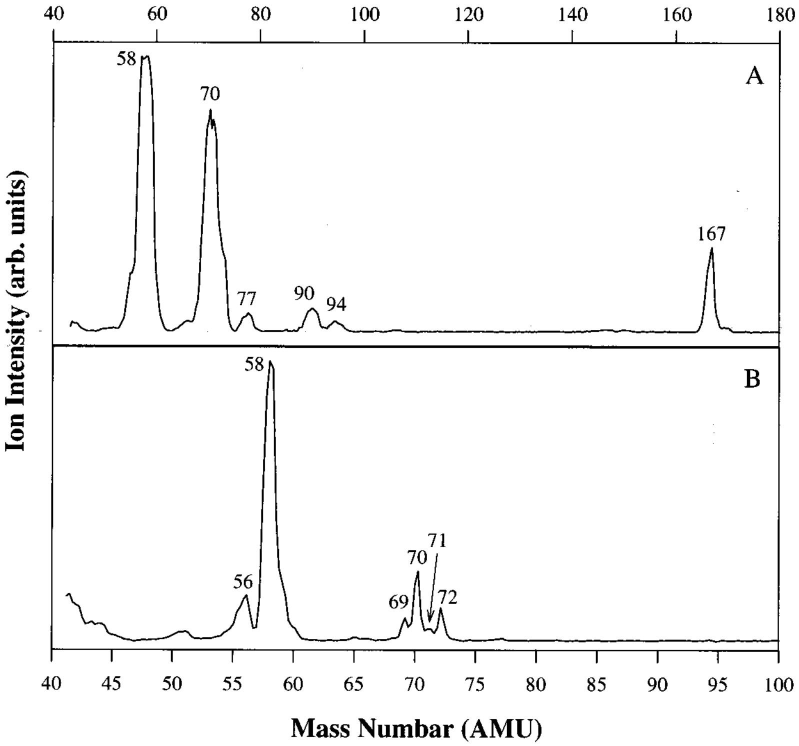


Figure 2. (A) Low-resolution mass spectrum of phenol-BTMA complex upon REMPI. (B) High-resolution mass spectrum.

IAN-98.[10] Even though we started the calculation with several initial geometries all of them converged to the same structure, which is given in Figure 1C. The ZPE and BSSE corrected stabilization energy of this complex was found to be −4.44 kcal/mol. In this structure, the phenolic proton is interacting with two hydrides on boron forming a pair of bifurcated dihydrogen bonds. The H····H contact distances are 1.87 and 2.25 Å, with the corresponding B−H····H angles of 103.0° and 84.1° and O−H····H angles being 151.4° and 143.0°, respectively. Short H····H contact distances, strongly bent B−H····H angles, near linear O−H····H angles and bifurcated dihydrogen bonds observed in the present structure are consistent with the observed geometrical parameters in the crystals of several borane-amine adducts reported in the literature.[1] Furthermore, the calculated O−H stretching vibration, shown in Figure 1B, predicts 152 cm^{-1} shift to a lower frequency, which is in excellent agreement with the experimental shift of 143 cm^{-1}.

Figure 2A shows a low-resolution mass spectrum after one color $S_1 \leftarrow S_0$ REMPI of phenol-BTMA complex under mild focusing conditions of the laser. Apart from the parent ion signal at 167 AMU, intense signals at 58 and 70 AMU and weak signals at 77 and 90 AMU were observed. Surprisingly, the signal corresponding to phenol ion at 94 AMU was extremely weak. The mass spectrum was recorded by saturating the strongest signal at 58 AMU so that very weak signals can be observed. In the quadrupole mass filter employed in the current study, the time scale for ions to reach the detector after ionization region is of the order of few tens of microseconds, which is usually sufficient for the fragmentation process to be complete. Therefore, the relative abundance of various mass fragments reflects their relative stability. To determine the exact mass numbers of the fragments, a high-resolution spectrum was recorded, which is shown in Figure 2B. In this spectrum, the major peaks correspond to mass numbers of 72, 70, 58, and 56, however, signals corresponding to weak peaks in Figure 2A could not be observed. The observed intensity differences in the two spectra are due to saturation of signal at 58 AMU in the low-resolution mass spectrum (Figure 2A). Additionally, in Figure 2B mass signals corresponding to 71 and 69 AMU, which are about 20% intensity with respect to peaks at 72 and 70 can also be seen. This indicates presence of boron in these fragments because the isotopes ^{11}B and ^{10}B are in the ratio 8:2.[11]

To determine the origin of observed fragments, mass resolved excitation spectra were recorded by monitoring each of the observed mass signal. Traces A−E in Figure 3 are the mass resolved excitation (action) spectra recorded by monitoring the parent ion, 72, 70, 58, and 56 mass signals, respectively. Also shown in Figure 3 is the LIF excitation spectrum (Trace F) for comparison. Higher background in mass resolved excitation spectra is due to higher laser power used in comparison with LIF excitation spectrum. All of the spectra shown in Figure 3 are in good agreement with each other within the experimental uncertainties. This establishes that all the mass fragments originate from the phenol-BTMA complex. Further, BTMA in the absence of phenol showed no mass signals under identical experimental conditions. This reiterates that all the mass fragments originate from the parent complex ion.

Most of the hydrogen bonded complexes of phenol, depending upon their structure, fragment upon ionization in moderate to intense laser powers. Phenol cation is the major fragment in all the cases including the dihydrogen bonded phenol-BDMA complex. The only known exception to this is the phenol-trimethylamine complex, wherein a proton transfer occurs from phenol to trimethylamine following ionization. In that case, the mass spectrum shows weak parent complex ion signal and an intense protonated-trimethylamine $[HN(CH_3)_3^+]$ signal, and no signal corresponding to phenol cation.[8] In the present case, the extremely weak signal of phenol is believed to be due to broad background in the mass resolved and LIF excitation spectra (Figure 3) and not from directly from the fragmentation of the phenol-BTMA parent ion. Even, in the event of phenol ion being produced by fragmentation of phenol-BTMA complex ion, its cross-section is very low and would not alter the ensuing discussion. The absence (or very small amount) of phenol signal

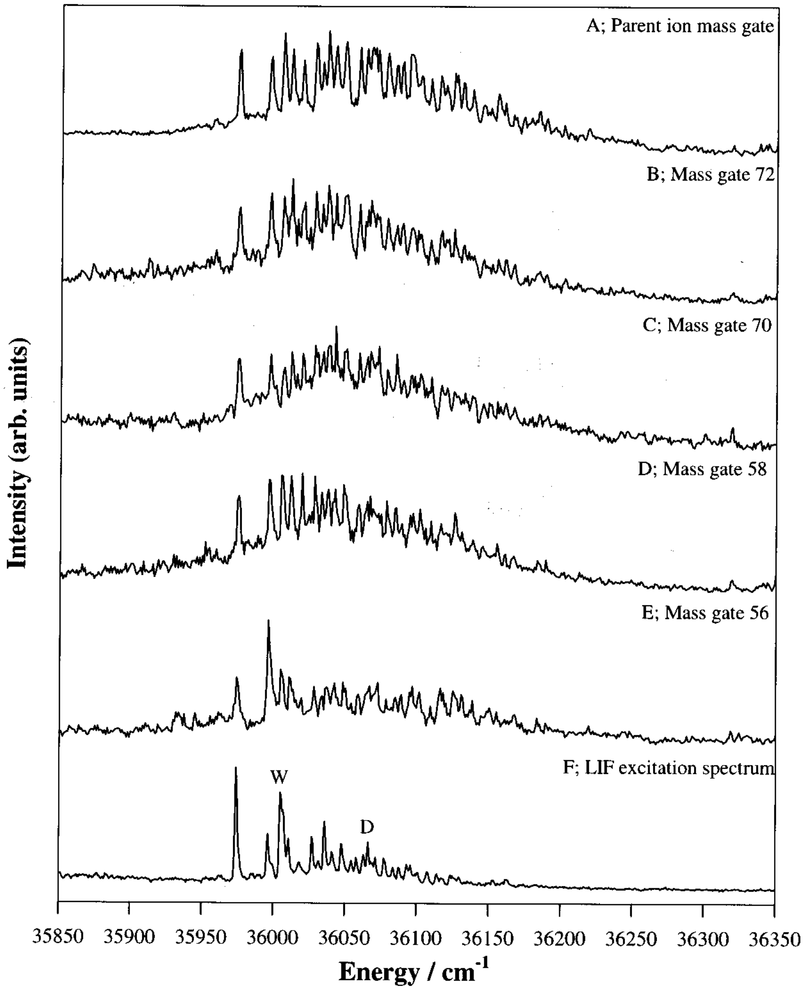


Figure 3. Traces A−E are the mass resolved S1 ← S0 excitation (action) spectra of phenol-BTMA complex with mass gates at 167, 72, 70, 58, and 56 AMU. Trace F is the LIF excitation spectrum. Peaks marked W and D in the LIF excitation spectrum are due to phenol-H_2O and phenol dimer, respectively.

upon photoionization of phenol-BTMA complex has a striking similarity in the mass spectral characteristics with that of phenol-trimethylamine complex. This suggests proton transfer from phenol to BTMA in the complex ion.

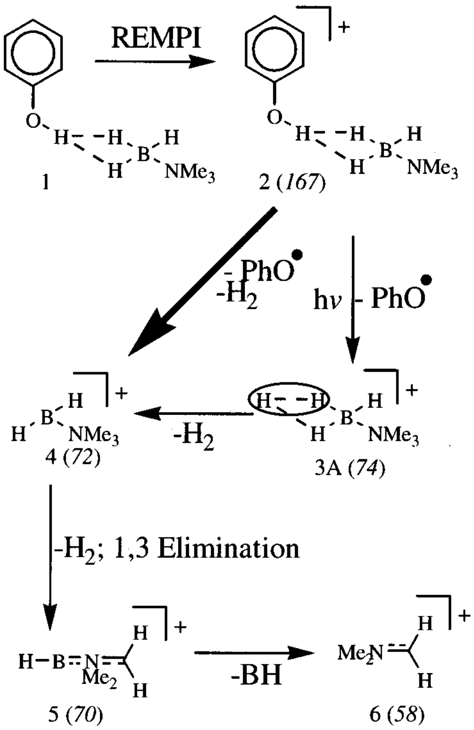
Scheme 1 is proposed to explain the observed mass spectral pattern. In this scheme the phenol-BTMA complex, **1** (schematic representation of Figure 1C), absorbs an additional photon upon ionization (this was ascertained by the fact that under divergent or low laser power conditions no fragmentation was observed) generating a very high internal energy complex ion, **2**, which subsequently fragments. As mentioned earlier, the absence of phenol following the fragmentation of the parent complex, suggests a intracluster proton transfer from phenol to BTMA. This would therefore, lead to 74 mass fragment, **3A**, which, however, was not observed. On the other hand, we observe mass 72 (**4**), which is one mass unit less than BTMA. Subsequent fragmentation leading to mass fragments 70 (**5**), 58 (**6**), and 56 AMU can be rationalized,[12] as illustrated in scheme 1. In the present case, the absence of 74 mass signal might be due to very high internal energy in the phenol-BTMA complex ion. In an attempt to reduce the internal energy of the complex, we carried out two-color REMPI, in which the first photon (ν_1) was in resonance with the band-origin transition of the complex at 35 964 cm^{-1}. The laser power was kept very low to avoid ionization. The second color laser(ν_2) was used to ionize and subsequently photofragment. The lowering of ν_2 energy from from 35 964 cm^{-1} (278 nm) to 29 850 cm^{-1} (335 nm) (approximately to 1.5 eV) did not change the mass spectral pattern and the signal at 74 AMU was not observed. This may be due to the fact that, even with ν_2 at 29 850 cm^{-1} the amount of internal energy in the complexes ion is considerable. However, further reduction of ν_2 was not feasible due to large reduction of ion signal below 29 850 cm^{-1}.

Sato and Mikami[13] have shown that in the case of hydrogen bonded clusters of phenol, the intracluster proton-transfer reaction illustrated as

$$C_6H_5OH^+\cdots\cdot X \rightarrow C_6H_5O\cdots\cdot HX^+ \qquad (1)$$

would be feasible only if the proton affinity of X is about 205 kcal/mol or greater. The proton affinity of trimethylamine is 227 kcal/mol,[14] and hence, a facile proton transfer occurs from phenol to trimethylamine in the complex ion. In the case of phenol complexes with various proton acceptors, such as H_2O, MeOH, NH_3, and a variety of amines, a linear correlation exists between the proton affinity of the solvent with the red shift in the electronic transition and shift in the O−H stretching vibration to a lower frequency of phenol moiety. In the case of phenol-BTMA, both the red shift in electronic transition and the shift in the O−H stretching vibration to a lower frequency are higher than those of phenol-H_2O complex and lower than phenol-MeOH complex. Therefore, the proton affinity of the dihydrogen bonding site of BTMA should lie between the 165 kcal/mol[14] (H_2O) and 180 kcal/mol[14] (MeOH) and can be roughly estimated

SCHEME 1: Mechanism Showing Fragmentation of Phenol-BTMA Complex Ion. The Italicized Numbers in Parenthesis Are the Mass Numbers of the Corresponding Fragment

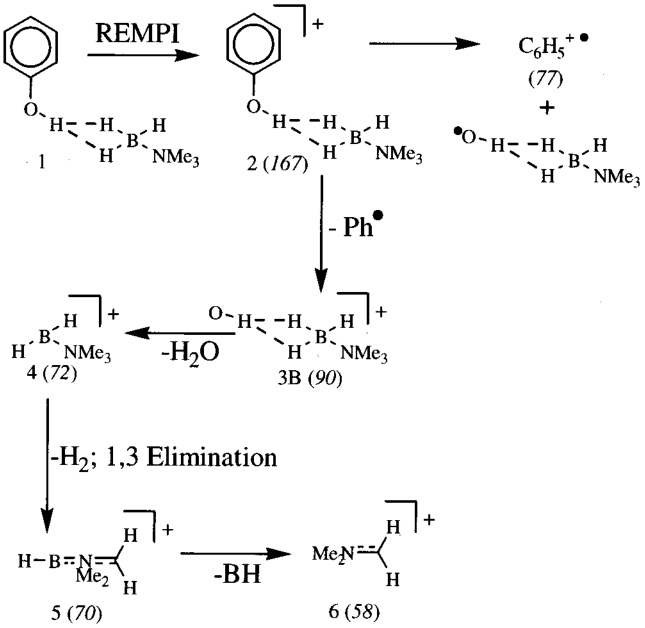


as ~168 kcal/mol. Because the proton affinity of BTMA is very much less than the value required for the reaction 1 to proceed toward right-hand side, the proton transfer from phenol to BTMA can be ruled out. This justifies the absence of signal at 74 AMU. From the mass spectrum, it can also be seen that apart from phenol moiety, BTMA also loses a hydrogen atom. Therefore, it is realistic to assume a three-body dissociation process of phenol-BTMA complex ion leading to elimination of phenoxy radical and molecular hydrogen as depicted by bold arrow in scheme 1.

An alternative scheme, Scheme 2, can also be considered to explain the observed mass spectral pattern. In the low-resolution mass spectrum (Figure 2A), a signal at 77 AMU ($C_6H_5^+$) arises due to C−O bond fission. Also seen is its counterpart $OHBH_3N(CH_3)_3^+$ at 90 AMU, **3B**. Fragmentation of $OHBH_3N(CH_3)_3^+$ leading to 72 mass would be possible only by elimination of H_2O. Further fragmentation is same as in scheme 1 and does not warrant any discussion. One of the most amazing facts of this scheme is, it originates from C−O bond fission, which has not been observed either in the case of bare phenol, in several other hydrogen bonded complexes, and in the phenol-BDMA dihydrogen bonded complex studied in this laboratory. Moreover, to the best of our knowledge, there is no report on the C−O bond fission in phenol complexes, and this is first such observation.

It can be seen from Figure 2 that the intensities of mass fragments 94 and 77 containing phenyl ring are very low compared to the rest of the fragments. This implies that charge transfer from phenyl ring to BTMA moiety is the primary process following ionization, which is the origin of both the schemes. In the electron impact ionization of phenol, the signals at 77 and 17 AMU following C−O bond fission are almost nonexistent,[15] even though the electron energy of 70 eV, which is much higher than ~12 eV in the present case and would generate many more excited electronic states. The C−O bond fission in the scheme 2 leads to an interesting situation of breaking the bond, which is not the weakest bond in the molecule. Therefore, it can be safely concluded, that the C−O bond dissociation channel (Scheme 2) is a minor channel relative to Scheme 1. Therefore, the major reaction channel, Scheme 1, is the three-body dissociation of parent complex ion with elimination of phenoxy radical and molecular hydrogen. This is the dehydrogenation reaction from the dihydrogen bonded phenol-BTMA complex following photoionization. With regard to C−O bond fission, presently, we do not have any plausible explanation for such a process.

SCHEME 2: An Alternative Mechanism Showing Fragmentation of Phenol-BTMA Complex Ion. The Italicized Numbers in Parenthesis Are the Mass Numbers of the Corresponding Fragment



IV. Conclusion

The photofragmentation of the dihydrogen bonded phenol-BTMA complex following REMPI suggests the proton transfer from phenol to BTMA. From the spectral shifts in the electronic as well as O−H stretching transitions of phenol-BTMA complex, the proton affinity of dihydrogen bonding site of BTMA was estimated as 168 kcal/mol, which is much less than that required for the proton transfer from phenol. The observed fragmentation pattern in the mass spectrum indicates a three-body dissociation of phenol-BTMA complex ion leading to the dehydrogenation reaction. Finally, C−O bond fission channel was observed for the first time in phenol complexes.

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