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GAS-PHASE REACTIONS OF V$^+$ AND VO$^+$ WITH METHANOL

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The reactions of V$^+$ and VO$^+$ with methanol have been investigated experimentally by FT-ICR mass spectrometer and theoretically by ab initio calculation. Both V$^+$ and VO$^+$ exhibit impressive reactivity with methanol. The products distribution of different reaction time indicate that in whole reaction processes methanol is adsorbed one by one, and no more than four methanol molecules can be solved in the first shell of central ion V$^+$. The reaction mechanisms have been proposed, and the possible geometrical structures of products are also analyzed by DFT calculations.

Keywords: Reactivity; FT-ICR mass spectrometer; ab initio calculation.

1. Introduction

Gas-phase reactions of "bare" transition metal ions with small organic molecules have attracted considerable attentions[1,2], because the gas-phase offers a unique possibility to probe the intrinsic properties of reactive organ metallic species[3], and the studies of reactions of cluster ions with small organic molecules may aid researchers in uncovering the mechanism governing certain catalytic processes, allowing for the development of more selective and efficient catalysts[4].

The transition metal vanadium cluster cation V$_n^+$ and their oxides have been widely applied in many industrial processes as heterogeneous catalytic supports[5]. Mang reports concerning the reactions of V$_n^+$ and their oxides ions with small molecules[6,7,8,9,10,11], but all these reports are mainly focus on the primary reactions, and do not relate to the reactions of primary products.

Methanol often be used to clarify the reaction activity of ions[12,13,14], and it also has potential to be a possible alternative fuel source[15]. In fact, although vanadium

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cluster cation, vanadium oxide cluster cations and methanol have been widely applied and studied, there is a lack of fundamental understanding of the complicated processes. Therefore, the researches of the reactions of V^+ and VO^+ with methanol are needed required. The primary reactions of the methanol with V^+ and VO^+ have been studied experimentally and theoretically[16]. In this paper, our interest is to investigate the reactions of V^+ and VO^+ with methanol after the primary reactions.

2. Experimental Procedure

The experiments are performed on a Bruker Fourier transform ion-cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source. Briefly, the metal cations are generated by focusing the beam of a Nd:YAG laser (home made, λ=532 nm) onto a metal or metal oxide target. All of the cations are transferred to the analyzer cell. The ions in the analyzer cell are firstly thermalized by nonreactive collisions with pulsed-in argon buffer gas, and then react with methanol. Some CID experiments are performed to speculate the structure of some ions.

3. Experimental Results and Discussion

The reactions of V^+ and VO^+ with methanol at different reaction time are performed, and the detailed experimental results are list in table 1. The following properties can be gotten from the data in table 1: First, V^+ and VO^+ exhibit an impressive reactivity towards methanol, and some products located between $[VO_2H_2^+]$ and $[VO_3C_3H_{10}^+]$. Second, with the reaction time prolongs, the products of large mass will produce and the products of light mass will decrease or disappear. Third, the largest mass product observed in the reaction of VO^+ with CH_3OH is $[VO_4C_4H_{12}^+]$, while the largest mass product of V^+ with CH_3OH is $[VO_4C_4H_{13}^+]$. Fourth, it should be noted that the relative intensity of $[VO_3C_3H_{10}^+]$ is much higher than other products with longer reaction time. Considering the products of different reaction time, it can be deduced that no more than four methanol molecules can be solved in the first shell of the central ion V^+, although $[VO_4C_4H_{13}^+]$ is not observed in the reaction of VO^+ with CH_3OH at present.

In order to deeply study the dominant products, some CID experiments are performed. The main loss fragments of $[VO_3C_3H_{10}^+]$ are H, CH_3, CH_3OH and CH_3OCH_3. Comparing the CID experimental results between $[VO_3C_3H_9^+]$ and $[VO_3C_3H_{10}^+]$, it can be seen that $[VO_3C_3H_9^+]$ is devoid of the first dehydrogenated step from $[VO_3C_3H_{10}^+]$ to $[VO_3C_3H_9^+]$. The first dissociation product of $[VO_4C_3H_{10}^+]$ is $[VO_3C_3H_{10}^+]$, then the following dissociation products are the same with that of $[VO_3C_3H_{10}^+]$. So it can be induced that the larger mass product $[VO_4C_3H_{10}^+]$ comes from the reaction of $[VO_3C_3H_{10}^+]$ with methanol.

The mechanism for reactions between VO^+ with methanol is listed in figure 1, in which the ligand OCH_3 of the methanol is expected to attack VO^+ ion. $[CH_3O\text{-}M^+\text{-}OH]$ and $[CH_3O\text{-}M\text{-}OCH_3^+]$ are the important intermediate products. The simple

adsorption reactions, the dehydration and dehydrogen reactions play an essential role in whole processes. In current experiment condition, $[VO_3C_3H_{10}^+]$ is the main product in all the reactions, and this is similar to the reactions of Sc^+, Y^+ and $Lu^+$with methanol[17]. So it could be conclude that all these reactions are the continuous adsorption processes of single methanol.
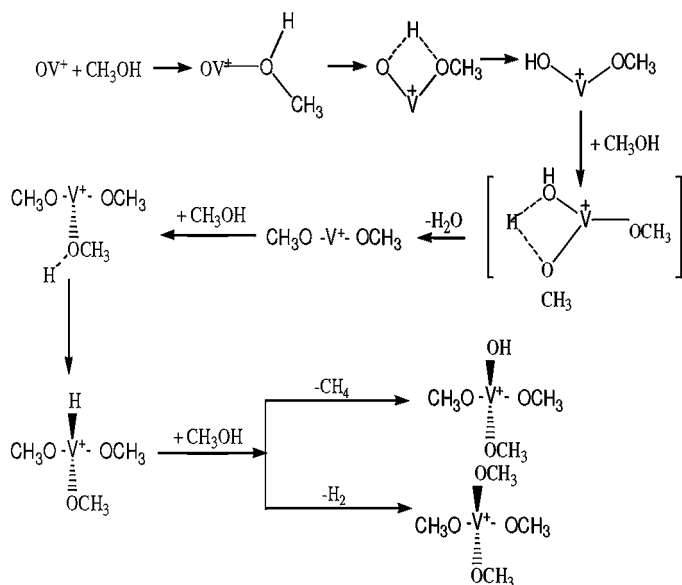
Table 1: Relative intensity in % of products at different reaction time, and the relative intensity at each reaction time is normalized.

Products	V^++CH_3OH					VO^++CH_3OH				
	0.2s	1.0s	2.0s	5.0s	10.0s	0.2s	1.0s	2.0s	5.0s	10.0s
V^+	88.0	49.2	30.8							
VO^+	3.6	14.4	19.5			80.5	50.2	39.3	29.0	
VOH^+	6.0	25.4	24.9							
VO_2^+						1.2			2.0	
$VOCH_3^+$	2.4	9.3	14.6						1.2	
$VO_2CH_2^+$						7.6	9.6	8.4	5.9	
$VO_2H_2^+$						0.7				
$VO_2CH_4^+$		1.7	4.9			9.3	31.2	34.1	27.4	1.8
$VO_2C_2H_6^+$			1.6		3.2	0.7	5.0	11.2	11.8	3.2
$VO_2C_2H_8^+$			3.7	5.2	5.3		1.2		1.7	2.8
$VO_3C_2H_6^+$				12.0	1.4	0.8	3.0	3.8	3.6	
$VO_3C_2H_8^+$				5.1	2.2	0.5	1.2	5.9	1.0	
$VO_3C_3H_8^+$									1.2	4.8
$VO_3C_3H_9^+$				14.6	16.0	0.2	1.0	1.7	18.2	
$VO_3C_3H_{10}^+$				46.9	60.2	1.3	1.8	8.4	45.8	
$VO_3C_3H_{11}^+$				3.1						2.4
$VO_4C_3H_{10}^+$				4.7	11.7					10.8
$VO_4C_4H_{12}^+$				6.8						5.6
$VO_4C_4H_{13}^+$				1.6						

4. Calculation Method and Results

The geometries of the reaction products are fully optimized at the level of B3LYP/DZVP. To characterize the nature of the stationary points, harmonic vibrational frequencies are also calculated with the method mentioned above. Some test calculations are performed, and our calculation results are in good agreement with experimental estimations[18],and which suggests that the B3LYP method coupled with DZVP basis set are suitable for the purpose of the present study. All the calculations are carried out with Gaussian 98 program suite.

The optimized geometries of the reaction intermediates are shown in figure 2. All these points are local minima on the potential energy surface except $[VO_3C_3H_{10}^+]$ C. Configuration $[VO_3C_3H_{10}^+]$ C has one image frequence, but it is small.

$$OV^+ + CH_3OH \longrightarrow OV^{\pm}\!\!-\!O\!\!-\!CH_3 \longrightarrow O\!\!-\!\!V^+\!\!-\!OCH_3 \longrightarrow HO\!\!-\!\!V^+\!\!-\!OCH_3$$

$$+CH_3OH$$

$$\left[\; HO\!\!-\!\!V^+\!\!-\!OCH_3 \;\right]$$

$$CH_3O\!\!-\!\!V^+\!\!-\!OCH_3 \xleftarrow{+CH_3OH} CH_3O\!\!-\!\!V^+\!\!-\!OCH_3 \xleftarrow{-H_2O}$$
$$\underset{H}{\overset{OCH_3}{|}}$$

$$CH_3O\!\!-\!\!V^+\!\!-\!OCH_3 \xrightarrow{+CH_3OH} \begin{array}{c} \xrightarrow{-CH_4} CH_3O\!\!-\!\!V^+\!\!-\!OCH_3 \quad (OH,\ OCH_3) \\ \\ \xrightarrow{-H_2} CH_3O\!\!-\!\!V^+\!\!-\!OCH_3 \quad (OCH_3,\ OCH_3) \end{array}$$

Fig. 1.   The mechanism for reactions VO^+ with methanol

[**VOH**$^+$] Concerning the structure of the VOH$^+$ ions, it is clear that the metal hydroxide isomer V$^+$-OH is more stable than the hydride-oxide O-V$^+$-H species since the O-H bond is much stronger than V-H bond.

[**VO$_2$H$_2^+$**] The symmetrical dihydroxide-metal structure HO-V$^+$-OH is preferable to the water- vanadium oxide H$_2$O-VO$^+$ isomer.

[**VO$_2$CH$_4^+$**] The structures A, B and C listed in figure 2 may coexist in an equilibrium mixture of [VO$_2$CH$_4^+$]. Considered from electronic, thermodynamic and mechanistic arguments, structure B is more suitable for [VO$_2$CH$_4^+$] product. First, in isomer A, the dative interactions exist between the metal ion and ligands, and the bond length of V-O is 2.07Å, so this interaction is very weak. Secondly, it is well known that for early transition metal ions, s and d orbitals with maximum charge density may exist at 90 angle. This hybridization is ideal while forming two covalent bonds as in structure B. Thirdly, previous work has demonstrated that the reaction mechanism of H$_2$ or alkyl-H with VO$^+$ involves initial oxidative addition of H$_2$ or alkyl-H to the metal center, then followes by H or alkyl group migration to the oxygen[19,20]. We believe that structure B is more favorable in experiments, although our calculation results shown isomer A is more stable. Isomer A is the possible primary product and it will change to isomer B by migrating H to another oxygen under the single- as well as multiple-collision conditions.

[**VO$_2$C$_2$H$_6^+$**] Two possible structures A and B listed in figure 2 are allowed for [VO$_2$C$_2$H$_6^+$]. According to the energetic arguments discussed above for [CH$_3$OVOH$^+$], [VO$_2$C$_2$H$_6^+$] may prefer isomer A [CH$_3$O-V-OCH$_3^+$] to isomer B. Our calculation results show structure A is more stable than complex B by 30.4 kcal/mol, and the V-O bond length of V and O(in methanol group of [CH$_2$O-V-

OHCH$_3^+$]) is 2.07Å, which suggests that only the weak dative interaction exists between the metal ion and ligands.
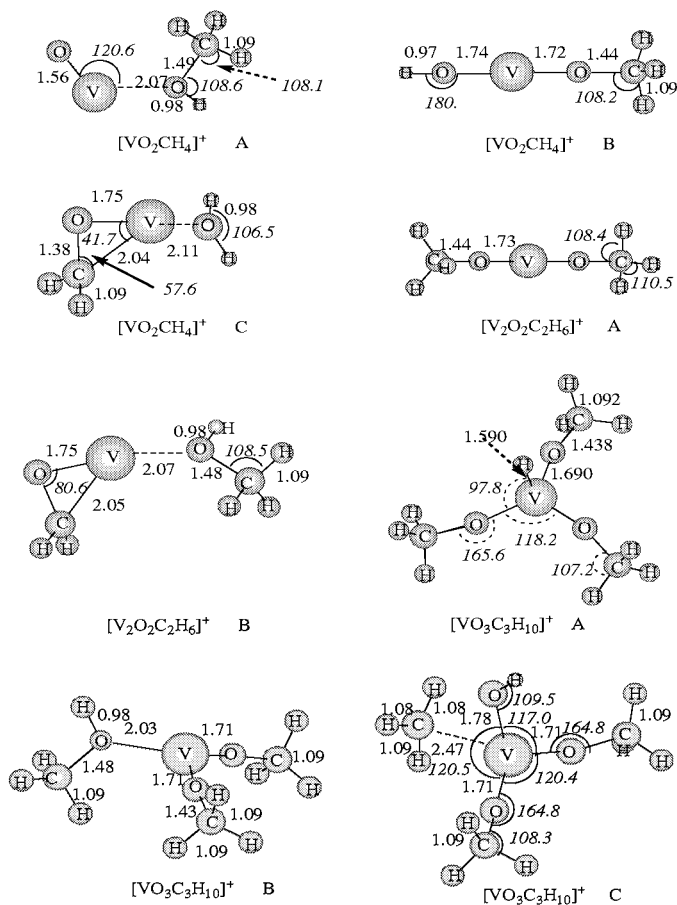

Fig. 2. Optimized structures for the intermediates and products. Bond distances and angles (indicated in italic) are in units of Å and degree, respectively.

[**VO$_3$C$_3$H$_{10}^+$**] Many possible isomers of [VO$_3$C$_3$H$_{10}^+$] might exist, and three are considered in this paper. The most stable one is the configuration A [V(OCH$_3$)$_3$H$^+$], where three OCH$_3$groups reside around the metal cation V$^+$in different sides, and H atom bonds to V$^+$directly. This configuration is C$_3$ symmetry, and the four coelectrons of central V$^+$ have bond fully, that is, three are bonded to O and the last one is bonded to H. Configuration B is C$_1$ symmetry, and is 8.03 kcal/mol higher in total energy than configuration A. Configuration C is C$_S$ symmetry, and is 24.0 kcal/mol higher in total energy than configuration A. So structure A is more favorable in experiments. Isomer B is the primary product and it will change to isomer A by migrating H to V$^+$.

5. Conclusion

Employing FT-ICR mass spectrometer and DFT calculation, we have studied the reactions of V^+ and VO^+ with methanol. The main results can be summarized as follow: V^+ and VO^+ are much more reactive toward methanol. $[VO_4C_4H_{13}^+]$ and $[VO_4C_4H_{12}^+]$ are the largest mass product of in the reaction of V^+ with CH_3OH and VO^+ with CH_3OH respectively. The important product $[VO_3C_3H_{10}^+]$ could be assigned to $[V(OCH_3)_3H]^+$. No more than four methanol molecules can be solved in the first shell of the central ion V^+. The mechanism for reactions from VO^+ to $[VO_4C_4H_{12}^+]$ and $[VO_4C_4H_{13}^+]$ are proposed, in which methanol is adsorbed one by one. DFT studies show the ground state configurations of the products in the reactions. The CID experiment results confirm the speculation.

Acknowledgments

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