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Reactions of M^+ and MO^+($M = V$, Nb, Ta) with methanol

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Abstract

The primary reactions of the transition metal cations M^+ ($M = V$, Nb and Ta) and their oxides with methanol are experimentally and theoretically investigated. Combining with the experimental results, we propose the reaction pathways of those primary reactions. The potential energy surfaces (PES) of these reactions are explored at B3LYP/Lanl2dz (for M) and 6-31g* (for C, H and O) level. The structures and properties of the complexes involving in these reactions are also theoretically studied. The calculated results show that a crossing between the high-spin and low-spin PES occurs just after TS1, which plays an important role in decreasing the barrier heights of these transition states. The theoretical results are in excellent agreement with the experimental results.

Keywords: Transition state; DFT; Reaction pathway

1. Introduction

As heterogeneous catalytic supports, the bare transition metal and their oxides have been widely used in many industrial processes, so the gas-phase reactions of ‘bare’ transition metal ions with small organic molecules have aroused considerable attention [1–3]. Without any solvent, ion-pair and other ‘bulk’ effects, the gas-phase reactions can offer a unique possibility to probe the intrinsic properties of reactive organometallic species, and the details of activate C–H and C–C bonds in the initial steps are of fundamental interest in catalysis [4–7].

The transition metal ions and their oxide ions are reactive for many organic substrates because their valence electron configurations lead the metal ions insert into organic bonds [8]. There have been a lot of reports concerning the reactions of metal and their oxides with organic molecules [1–21], especially the group V transition metal ions $V^{[+]}$, Nb^+, Ta^+ and their oxides for their industrial applications [1,9–17]. Methanol is one of the important organic molecules on clarifying the reaction activity of ions, because it can not only react with the main group element ions, alkaline earth metal ions, but also the transition metal element ions and lanthanide cations in the gas [22–27]. On the other hand, methanol has much effect of industry, for a large variety of chemicals are now produced from methanol as a starting material. It appears, therefore, that there is a need for further work involving the reactions of V^+, Nb^+, Ta^+ and their oxides with methanol.

In this paper, the primary reactions of M^+($M = V$, Nb and Ta) and their monoxide with methanol are investigated by both experiment and theory. Special attentions are concentrated on the reaction mechanism and energetic. The experimental results are in good consistent with high-level ab initio theoretical studies.

2. Experimental results and reaction mechanism

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 via laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (home-made, $\lambda = 532$ nm) onto a metal or metal oxide target. All cations are transferred to the analyzer cell, located within a 4.7-Tesla superconducting magnet. The interested ions are selectively isolated by frequency sweep excitation–ejection technique [28] in the analyzer cell,

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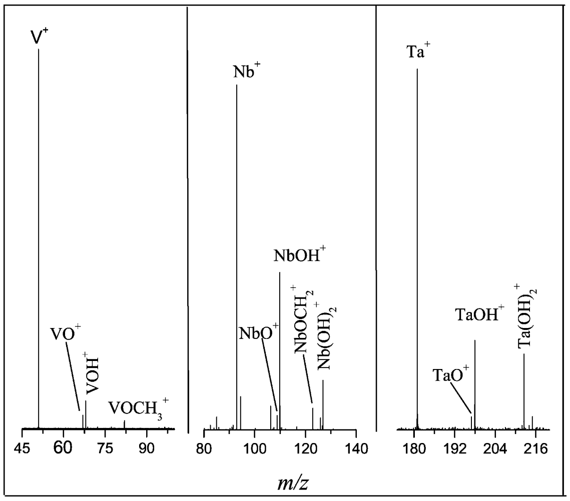


Fig. 1. Typical mass spectrum showing the reaction products of V^+, Nb^+ and Ta^+ with methanol.

then react with pulsed-in methanol vapor gas at the pressure ranging from 5×10^{-8} to $5 \times 10^{-}$ [10] mbar.

The mass spectrum in Fig. 1 shows the primary reaction products of V^+, Nb^+ and Ta^+ with methanol. Four reaction channels have been found.

$M^+ + CH_3OH \rightarrow MO^+ + CH_4$ Channel 1

$M^+ + CH_3OH \rightarrow MOH^+ + CH_3$ Channel 2

$M^+ + CH_3OH \rightarrow MOCH_2^+ + H_2$ Channel 3

$M^+ + CH_3OH \rightarrow MOCH_3^+ + H$ Channel 4

The dominant products MO^+ and MOH^+ can been observed in the reactions of these three metal cations generated by Channel 1 and Channel 2. Channel 3 and Channel 4 are fit for Nb and V, respectively. Small $NbOCH_2^+$ is formed in the reaction of Nb^+ with methanol, and $VOCH_3^+$ also can be observed in the reaction of V^+ with methanol.

The products of VO^+ with methanol are shown in Fig. 2. VO^+ is selected for reacting with pulsed-in methanol vapor gas. $VCH_4O_2^+$, $VCH_2O_2^+$ and VO_2^+ are the main products, and the relative intensities of $VCH_4O_2^+$ and $VCH_2O_2^+$ are much higher than that of VO_2^+. $V(OCH_3)_2^+$ and $V(OH)_2^+$ are the secondary reaction products of VO^+ with methanol, and will not be studied in this paper. Under the same condition, $TaHO_2^+$ is the only product in the primary reaction of TaO^+ with methanol. The relative intensity of NbO^+ is too small to be selected.

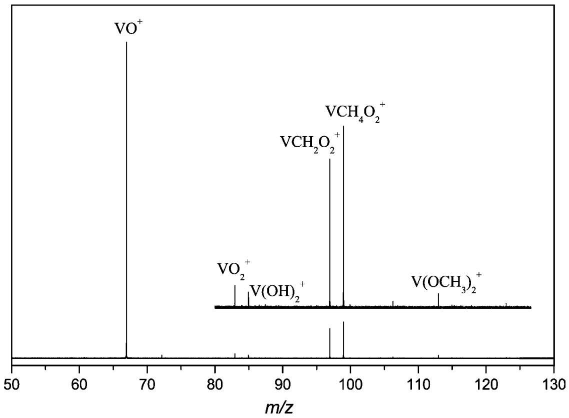
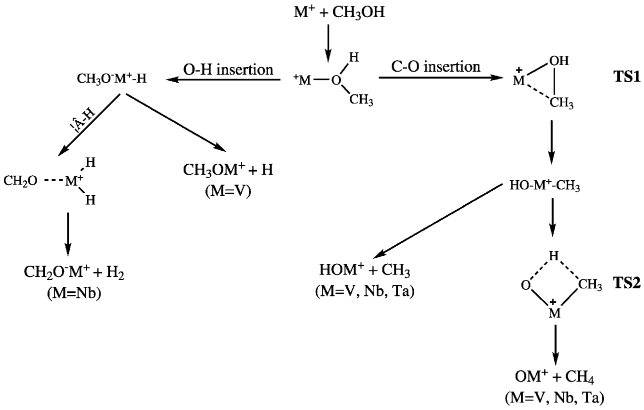


Fig. 2. Typical mass spectrum showing the reaction products of VO^+ with methanol. The inset mass spectrum is the enlarged parts.

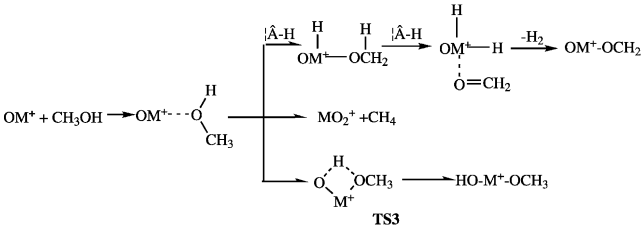


Scheme 1. The reaction pathway for V^+, Nb^+ and Ta^+ with methanol.

After analyzing the products of M^+($M = V$, Nb and Ta) and their oxides cations with methanol, the reasonable reaction schemes have been speculated, and they are listed in Schemes 1 and 2, respectively. The reaction schemes in present studies are supported by previous reports [18,29–32]. It is obvious that both the low-energy reaction pathway and the high-energy reaction pathway [31] appear in our experiments. M^+ is active towards C–O bond in the channel 1 and the channel 2, and is active to the O–H bond in the channel 3 and the channel 4, and all these products are produced by the dissociating attachment reaction. MO^+ is formed via the low-energy reaction pathway: the metal ion oxidatively inserts into the C–O bond of CH_3OH, and migrates the H atom of OH to CH_3 group, then reductively eliminates CH_4. MOH^+ are thought to arise from the high-energy reaction pathway, in which oxidative insertion and the simple bond cleavage are the dominant reaction processes.

As to the formation of $Nb^+–OCH_2$, Nb^+ inserts into the O–H bond, and then follows by a β-H shift and elimination of H_2. $VOCH_3^+$ is generated by the high-energy reaction pathway, in which V^+ inserts into the O–H bond firstly, and then follows by a H-elimination process.

In the reactions of VO^+ with methanol, the association reaction is the first step. The association complex [VO $(CH_3OH)]^+$ might generate TS3, and the reacting system



Scheme 2. The reaction pathway for VO^+, NbO^+ and TaO^+ with methanol.

passes it over to form the complex HO–V^+–OCH_3. $VO(CH_3OH)^+$ will take other two reaction channels to generate $VCH_2O_2^+$ and VO_2^+. In the first reaction channel, VO^+ will insert into the O–H bond firstly, and then $OVOCH_2^+$ will form by two times β-H transform and H_2 eliminate. While eliminating CH_4 group in the second reaction channel can produce VO_2^+.

3. Calculation method

All the calculations are carried out using Gaussian 98 program suite [34]. The geometries of the species involved in the reactions are fully optimized at the level of B3LYP calculation, which stands for a density functional theory (DFT) method using Becke's three parameter semiempirical exchange functional (B3) along with the Lee, Yang, and Parr (LYP) correlation functional [35]. The spin-restricted version of this methodology is used for the closed shell species, while an unrestricted approach is employed for all the open shell systems. Lanl2dz basis set is used for all transitional elements M(M = V, Nb, and Ta) and the 6-31g* basis set is used for C, H and O atoms. To characterize the nature of the stationary points, harmonic vibrational frequencies are calculated with the method mentioned above. All the stationary points are positively identified as local minima or as the transition state. In order to confirm that the transition state connected the designated complexes, the intrinsic reaction coordinate (IRC) [32–33] calculations also have been performed. For each species, the different states are considered.

To determine the suitability of the method and the basis sets for the systems studied here, some test calculations are performed. The results suggest that the B3LYP method coupled with Lanl2dz basis set for transitional elements and 6-31g* basis set for C, H and O should be suitable for present study. As to the higher-level method MP2, the structures optimized have little change while compared with the results of B3LYP method, but it cost much longer time. In the case of the higher-level basis set DZVP, the results are in good agreement with experimental estimations [36] for V and Nb, while there is no DZVP basis set for Ta. In order to keep the results in the same accuracy, and the main concern is to obtain the important potential energy surfaces (PES) along the reactions but not the detailed geometry optimizations, so the B3LYP mothod and Lanl2dz (for transitional elements), 6-31G* basis set (for C, H and O) have been used.

4. Theoretical results and discussions

4.1. The structures

It could be thought that many structural isomers might coexist for the reactants, intermediates, products, transition states, and other fragment species in the experimental studies. To get the most possible structures, the calculations at the B3LYP level are performed. The sketch maps of the configurations involving in the reactants of M^+ with CH_3OH are shown in Fig. 3. The ground states of all configurations of the complex in the reactions are quintet states. For the same configuration, the detailed geometrical parameters are approximate for different metals in the calculations. The structures of $[MOH]^+$, $[MOCH_2]^+$ and $[MOCH_3]^+$ most likely are the metal-hydroxide $[MOH]^+$, metal–formaldehyde complex $[MOCH_2]^+$ and metal-methoxide $[MOCH_3]^+$, respectively.

In the reactants M^+–CH_3OH system, M^+ is connected directly with the O atom of methanol. The C–O bond length in single methanol molecule is 1.410 Å, while it is 1.470 Å in V^+–CH_3OH, 1.460 Å in Nb^+–CH_3OH and 1.480 Å in Ta^+–CH_3OH. It changes by 0.05, 0.05 and 0.07 Å respectively. The C–H and H–O bond lengths in M^+–CH_3OH are nearly the same with pure methanol molecule, and this is consistent with that the metal cations insert into C–O bond to form HO–M^+–CH_3.

The transition states TS1 s are the three-member ring structures. They are verified to be the first-order saddle points on the PESs by their single imaginary frequencies: $590.1i$, $543.1i$ and $591.4i$ cm^{-1} of the quintet

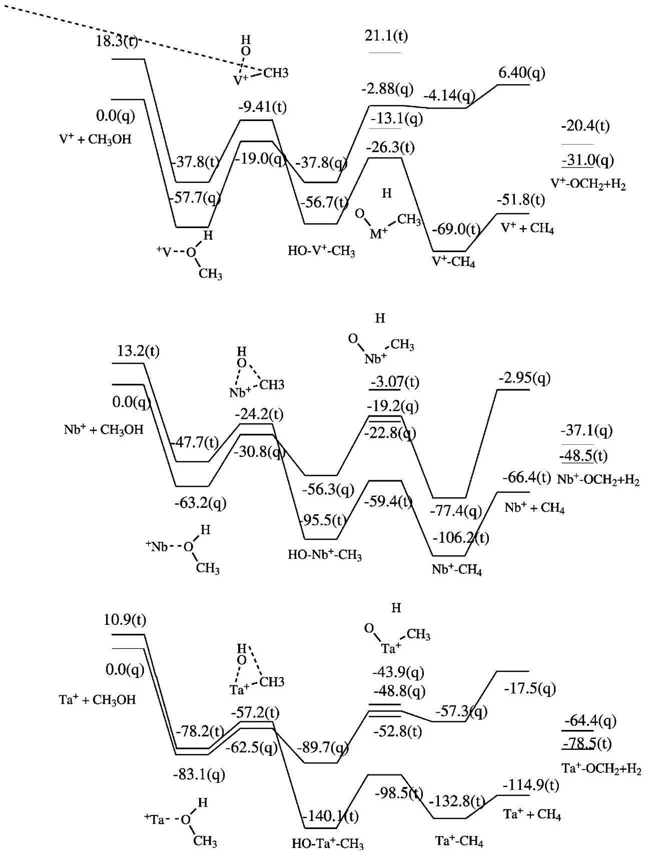


Fig. 3. Potential energy diagrams for the reaction of M^+ with CH_3OH (M = V, Nb, and Ta) in the high-spin and low-spin states. Relative energies are in kcal/mol.

state, and 560.7*i*, 490.5*i*, 508.6*i* cm^{-1} of the triple state for V^+, Nb^+ and Ta^+, respectively. The vibrational mode and the IRC analysis can confirm the migration of CH_3 from the O atom to metal atoms in TS1 s. The transition states TS2 are the four-member ring structures. They are characterized by single imaginary frequencies of 1637.2, 1648.7, 1640.8 cm^{-1} of V, Nb and Ta in their triple ground states respectively. Both the vibrational mode and the IRC analysis confirm that the TS2s are associated with the cleavage of O–H bond, and the migration of H from OH group to CH_3 group.

The sketch maps of the configurations involving in the reactants of MO^+ with CH_3OH are shown in Fig. 4. In the reactants $OM^+–CH_3OH$, M^+ is connected directly with the O atom of methanol like in the reactants $M^+–CH_3OH$. The M–O (M–O2) bond lengths are 2.020 Å, and 2.010 Å for V, Nb and Ta in the ground states, respectively. Comparing with $M^+–CH_3OH$ system, the M–O(M–O2) bond lengths change by 0.014 Å, 0.036 Å, and 0.06 Å for V, Nb and Tam, respectively. The C–O bond distances in $OM^+–CH_3OH$ are 1.470 Å, 1.470 Å, 1.510 Å, and they change by 0.06 Å, 0.06 Å and 0.10 Å, respectively. The H–O bond distances in $OM^+–CH_3OH$ are 0.975 Å, 0.974 Å 0.982 Å, and they have only little change by 0.006 Å, 0.005 Å and 0.013 Å, respectively when comparing with that of $M^+–CH_3OH$.

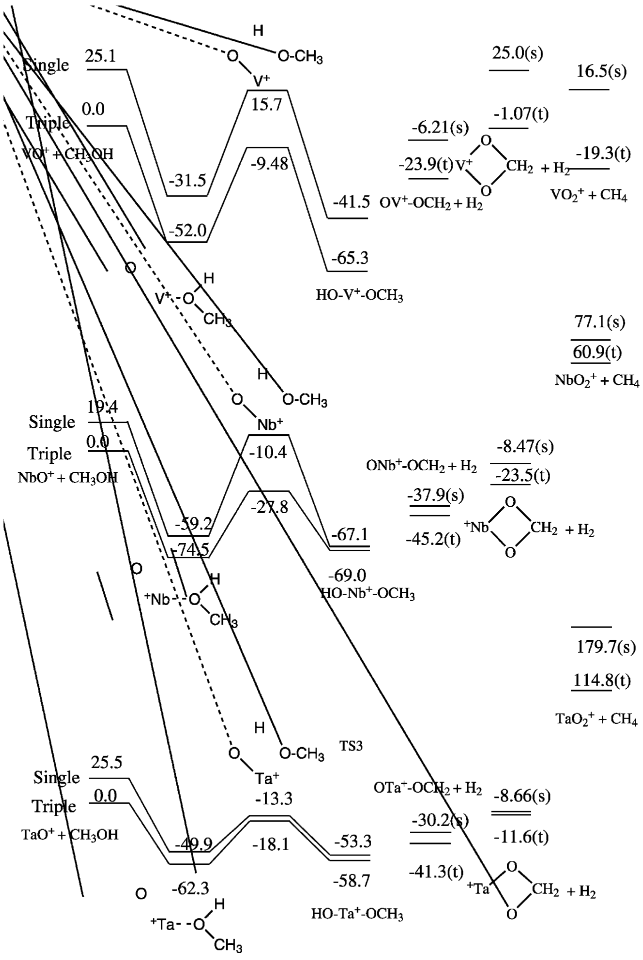


Fig. 4. Potential energy diagrams for the reaction of MO^+ with CH_3OH (M = V, Nb, and Ta) in the high-spin and low-spin states. Relative energies are in kcal/mol.

The structures of the transition state TS3s are verified to be first-order saddle points on the PESs by their single imaginary frequencies, 792.8*i*, 823.6*i* and 748.5*i* cm^{-1} of the single state, and 668.4*i*, 801.7*i*, 732.2*i* cm^{-1} of the triple state for VO^+, NbO^+ and TaO^+, respectively.

Two structures of $MO_2CH_2^+$(I) and $MO_2CH_2^+$(II) have been considered for $MO_2CH_2^+$ ion. Both MO_2CH_2 (I) and MO_2CH_2 (II) are the ground state structure, and MO_2CH_2 (I) is a four-member ring configuration, and MO_2CH_2(II) is a quasi-linear configuration. Considering the total energy and the PES, MO_2CH_2(II) is more favor in the present studies, but the possibility of MO_2CH_2 (I) cannot be excluded.

4.2. The potential energy surfaces (PES) for the reaction of M^+ and MO^+ with methanol

The reaction pathways between M^+ and the methanol have been discussed above. The PES for the high-spin(quintet) and low-spin state(triplet) reaction pathways for M^+ with methanol is shown in Fig. 3. The general profiles of these curves are downhill from the reactants to products. The overall reaction exothermic energies for V^+, Nb^+ and Ta^+ are − 40.2, − 67.1 and − 115.9 kcal/mol from the M^+/CH_3OH systems to MO^+/CH_4 systems, respectively, and are − 31.0, − 48.6 and − 78.56 kcal/mol to $M^+–OCH_2/H_2$ system. These processes are energetically favorable. Assuming only exothermic ion–molecule reactions can occur, it is expected that these reactions should easily take place. The calculation results are in good agreement with the experimental observations.

Since the PESs are same for the three metal cations, the V^+ as an example will be discussed here. The adsorption process between V^+ and methanol is highly exothermic by − 57.7 and − 37.8 kcal/mol in quintet and triplet states, respectively, which means the interaction between V^+ and methanol is very strong. The activation energy from $V^+–(CH_3OH)$ to $HO–V^+–CH_3$ via TS1s is 38.7 and 28.4 kcal/mol on the quintet state and the triplet state. The TS1 lies below the dissociation limit − 19.0 kcal/mol for the high spin ground states and − 9.4 kcal/mol for the low excited states.

It must note that there is a crossing between the high-spin state and the low-spin state energy surfaces for V^+ with methanol. The calculations strongly suggest a crossing just after the TS1s. A nonadiabatic electronic process-spin inversion is therefore expected to occur in the vicinity of the crossing part of the two PES. For the low-spin states of $HO–V^+–CH_3$, it is 18.9 kcal/mol lower than that for its high-spin states, and the low-spin states would energetically be more favorable. That is, the spin inversion would play an important role in the process from TS1s to $HO–M^+–CH_3$.

The activation energy from $HO–V^+–CH_3$ to $VO^+(CH_4)$ via TS2s is 30.4 kcal/mol on the low-spin ground state potential surfaces and 34.9 kcal/mol on the low-spin excited state potential surfaces, respectively. VOH^+/CH_3 of the ground state lies 38.6 kcal/mol above VO^+/CH_4 of the ground state, but it lies 13.2 kcal/mol below the dissociation limit. Thus V^+-OH species could be derived from the intermediate complex $HO-M^+-CH_3$ as shown in schem1 by a high-energy reaction process[35]. The calculation results have also shown that the overall energy is − 31.0 kcal/mol from V^+/CH_3OH to V^+-OCH_2/H_2 system, therefore this process is energetically favorable. And the overall energy change is − 48.5 kcal/mol from Nb^+/CH_3OH to Nb^+-OCH_2/H_2, and is − 78.5 kcal/mol from Ta^+/CH_3OH to Ta^+-OCH_2/H_2. That is, these processes are energetically favorable too.

In summary, the formation of MO^+ and MOH^+ are all energetically favorable in the present calculation results, and they have been observed in the present experiments. On the other hand, the formation of $MOCH_2^+$ is energetically favorable for M = V, Nb and Ta in the calculation, while only $NbOCH_2^+$ has been observed in the experiment. The discrepancy may probably be from the other factors involving in the reactions, since the reactions are not only controlled by thermodynamics, the kinetic factor must be taken into account [37]. The theoretical studies of $VOCH_2^+$ and $TaOCH_2^+$ will be helpful in the experimental detection.

The computed PES for the reactions from MO^+/methanol to MO_2^+/CH_4, $HO-M^+/OCH_3$ and $OM^+(OCH_2)/H_2$ in both low-spin and high-spin states are shown in Fig. 4. Similar to the reactions of M^+ with methanol, the general profiles for formations of $HO-M^+-OCH_3$ and OM^+-OCH_2 are downhill, and thus the corresponding reactions are energetically favorable.

The ground state for VO^+ is the triplet state, and the singlet state is energetically calculated to be 25.1 kcal/mol above. The association reaction of VO^+ with methanol is exothermic by 56.6 kcal/mol on the ground state. Then the reacting system can pass over TS3 to form the intermediate complex $HO-M^+-OCH_3$ using the high complexation energy. On the PESs, TS3 lies below the dissociation limits by 9.48 kcal/mol to VO^+ with methanol, therefore, the H–O bond should be easily cleaved. The formations of VO_2^+ and $O-V^+-OCH_2$ are energetically favorable by theoretical analysis, though it is slightly exothermic for VO_2^+. VO_2^+ and $O-V^+-OCH_2$ are both observed in the present experiments.

As to the reactions of NbO^+ and TaO^+ with methanol, the formation of both $ONb^+(OCH_2)/H_2$ and $OTa^+(OCH_2)/H_2$ are energetically favorable by the present theoretical analysis. But there is no $OTa^+(OCH_2)$ observed in the experiment. This divergence might be attributed to the experimental conditions. The formation of NbO_2^+ and TaO_2^+ are highly endothermic for NbO^+ and TaO^+ by 60.9 and 114.8 kcal/mol respectively, and there is no NbO_2^+ and TaO_2^+ observed in the experiments. The calculation results are consistent with the experimental results.

5. Conclusion

The reactions of the methanol with M^+ and $MO^+(M = V, Nb, \text{and } Ta)$ have been studied experimentally and theoretically The mass spectrum shows that for the reaction of M^+ with CH_3OH, the dominant products of the primary reactions are MO^+ and MOH^+, accompanying with fewer $Nb(OCH_2)^+$ and $VOCH_3^+$. It is concluded that the reaction pathway of methanol with M^+ is via transition states TS1 and TS2: $M^+ + CH_3OH \rightarrow M^+(CH_{3\text{-}}(CH_3OH) \rightarrow TS1 \rightarrow HO-M^+-CH_3 \rightarrow TS2 \rightarrow MO^+ + + + CH_4$, and the reaction pathway of MO^+ with CH_3OH is via a four-centered TS3. The calculation results also show that the reaction of M^+ with methanol is energetically favorable for all the three metal cations. Just after TS1, there is a crossing between the high-spin and low-spin PES, which plays a significant role in decreasing the barrier heights of these transition states. The energetic profiles for the reaction of MO^+ with CH_3OH have demonstrated that the formation of metal-dioxide is highly endothermic for NbO^+ and TaO^+, but it is slightly exothermic for VO^+. Our calculated results are in good agreement with the experimental results.

Acknowledgements

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References

[1] C.A. Schalley, R. Wesendrup, D. Schroeder, T. Weiske, H. Schwarz, J. Am. Chem. Soc. 117 (1995) 7711.
[2] D. Schroder, H. Schwarz, Anew. Chem. Int. Ed. Engl. 34 (1995) 1973.
[3] A. Luna, B. Amekraz, J.P. Morizur, J. Tortajada, O. Mo, M. Yanez, J. Phys. Chem. A 104 (2000) 3132.
[4] M.R.A. Blomberg, P.E.M. Siegbahn, U. Nagashima, Wennerberg, J. Am. Chem. Soc. 113 (1991) 424.
[5] R. Wesendrup, H. Schwarz, Organometallics 16 (1997) 461.
[6] K. Eller, H. Schwarz, Chem. Rev. 91 (1991) 1121.
[7] M. Pavlov, M.R.A. Blomberg, P.E.M. Siegbahn, R. Wesendrup, C. Heinemann, H. Schwarz, J. Phys. Chem. A 101 (1997) 1567.
[8] J. Collman, L. Hegedus, Principles and Applications of Organotransition Metal Chemistry, Mill Valley, CA, 1980.
[9] A. Bjarnason, D.P. Ridge, Organometallics 17 (1998) 1889.
[10] K.A. Zemski, R.C. Bell, A.W. Castleman Jr., Jr. Int. J. Mass Spectrom. 184 (1999) 119.
[11] W. Steven, R. Buckner, Marshall Pope, Int. J. Mass Spectrom. 182/183 (1999) 197.
[12] J.M. Lopez, G. Kremenic, J.L.G. Fierro, Appl. Catal. 61 (1990) 235.
[13] D.J. Hucknall, SelectiVe Oxidation of Hydrocarbons, Academic Press, New York, 1974, pp. 147–157.
[14] K. Mori, A. Miyamoto, Y.J. Murakami, Phys. Chem. 89 (1985) 4265.
[15] J.N. Harvey, M. Diefenbach, D. Schröder, H. Schwarz, Int. J. Mass Spectrom. 182/183 (1999) 85.
[16] K.A. Zemski, R.C. Bell, A.W. Castleman Jr., J. Phys. Chem. A 104 (2000) 5732.

[17] Q. Jiao Charles, D.R.A. Ranatunga, B.S. Freiser, J. Phys. Chem. 100 (1996) 4755.

[18] K. Yoshizawa, Y. kagawa, J. Phys, Chem. A. 104 (2000) 9347.

[19] Y. Shiota, K. Yoshizawa, J. Am. Chem. Soc. 122 (2000) 12317.

[20] R.A. Schldoon, J.A. Kochi, Metal Catalysed oxidation of Organic Compounds, Academic Press, New York, 1981.

[21] C.Y. Lee, R.G. Parr, Phys. Rev. B, 37 (1988) 785.

[22] M. Simoes, J.A. Beauchamp, Chem. Rev 90 (1990) 629.

[23] P.A.M. Van Koppen, P.R. Kemper, M.T. Bowers, in: B.S. Freiser (Ed.), Inorganometallic Ion Chem, Kluwer, Dordrecht, The Netherlands, 1996, p. 157.

[24] R.S. MacTaylor, W.D. Vann, A.W. Castleman Jr., J. Phys. Chem. 100 (1996) 5329.

[25] D. Vukomanovic, J.A. Stone, Int. J. Mass Spectrom. 202 (2000) 251.

[26] W. Lu, S. Yang, J. Phys. Chem. A. 102 (1998) 825.

[27] W. Lu, S. Yang, J. Phys. Chem. A. 102 (1998) 1954.

[28] S. Paul, J. Carolyn, Chem. Phys. Lett. 191 (1992) 111.

[29] M. Azzaro, S. Breton, M. Decouzon, S. Geribaldi, Int. J. Mass Spectrom. Ion Process. 128 (1993) 1.

[30] S. Geribaldi, S. Breton, M. Decouzon, M. Azzaro, J. Am. Soc. Mass Spectrom. 7 (1996) 1151.

[31] P.J. Robinson, K.A. Holbrook, Unimolecule Reactions, Wiley, New York, 1972.

[32] R.W. Jones, R.H. Staley, J. Phys. Chem. 86 (1982) 1669.

[33] S. Huang, R.W. Holman, M.L. Gross, Organometallics 5 (1986) 1857.

[34] D.A. Weil, C.L. Wilkins, J. Am. Chem. Soc. 107 (1985) 7316.

[35] C.Y. Lee, R.G. Parr, Phys. Rev. B, 37 (1988) 785.

[36] D.E. Clemmer, J.L. Elkind, N. Aristov, P.B. Armentrout, Phys. Rev. B 95 (1991) 3387.

[37] A. Burnin, J.J. BelBruno, J. Phys. Chem. A 107 (2003) 9547.

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Erratum

Erratum to “Reactions of M^+ and MO^+ (M = V, Nb, Ta) with methanol” [J. Mol. Struct.: THEOCHEM 683 (2004) 141–146]

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The Publisher regrets that errors occurred in the printing of Figs. 3 and 4 in the above paper. The correct figures now appear here.

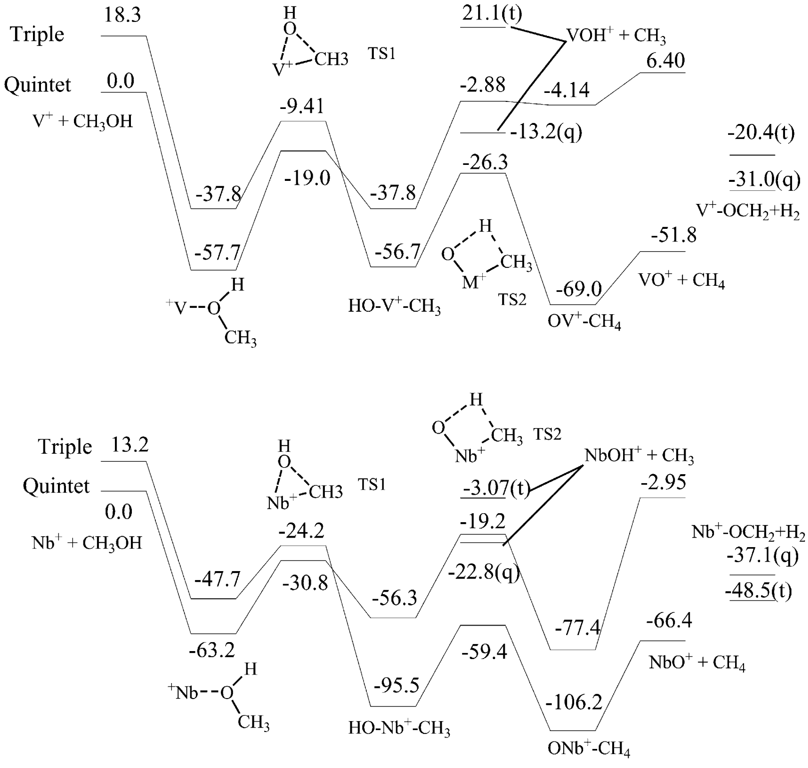

Fig. 3. Potential energy diagrams of the reaction M^+ with CH_3OH (M = V, Nb, and Ta) in the high-spin and low-spin states. Relative energies are in kcal/mol.

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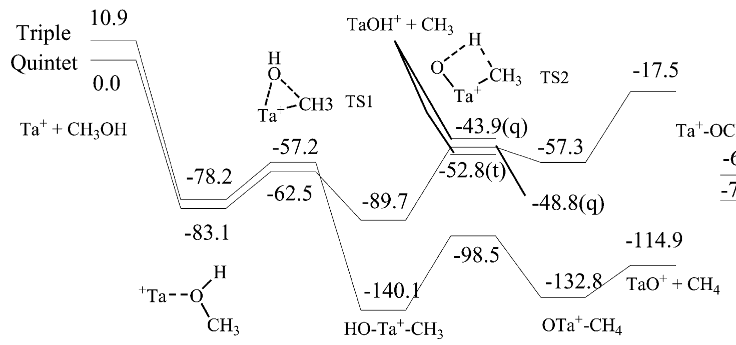

Fig. 3 (*continued*)

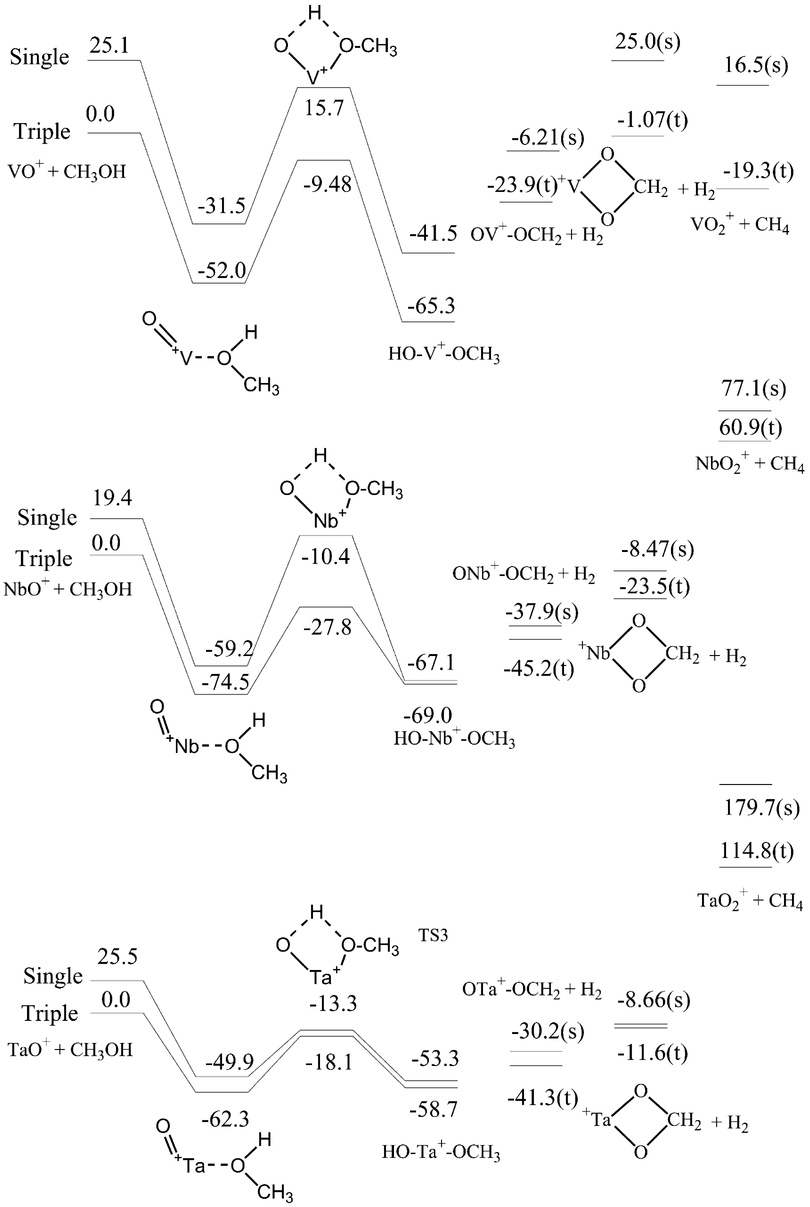

Fig. 4. Potential energy diagrams of the reaction MO^+ with CH_3OH (M = V, Nb, and Ta) in the high-spin and low-spin states. Relative energies are in kcal/mol.