ELSEVIER

Journal of Molecular Catalysis A: Chemical 153 (2000) 191–197

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Investigation of the energetics of the decomposition of methyl iodide on Ni(111) surface by the method of BOC–MP

Saied Azizian, Fereydoon Gobal *

Department of Chemistry, Sharif University of Technology, P.O.Box 11365-9516, Tehran, Iran

Received 21 January 1999; received in revised form 5 July 1999; accepted 13 September 1999

Abstract

The decomposition of methyl iodide on Ni(111) surface alone or in presence of hydrogen gives rise to the desorption of methane which appears as two peaks at two distinctly different temperatures (150 and 250 K) in the course of a temperature programmed desorption study (TPD). The method of bond order conservation–Morse potential (BOC–MP) analysis has been employed to rationalize the experimental findings by calculating the energies associated with the envisaged routes of the reactions. It is concluded that methyl groups adsorbed on 3-fold sites react with adsorbed hydrogen atoms with an activation energy of 14 kcal/mol to form gaseous methane desorbing at 250 K. The methyl group made mobile upon the crowdedness of the surface and traversing over on-top sites and having higher energy than the methyl groups adsorbed on 3-fold sites react with hydrogen with zero activation energy and forms the methane peak at 150 K in the TPD regime. The cleavage of C–I bond with an activation energy of 3 kcal/mol constitutes the rate determining step. The prediction capabilities of the method are further proven by briefly considering the process on Ni(100) and Ni(110) surfaces where in the former excellent agreement with the experimental findings is met and in the latter the theoretical findings are brought to the attention of the experimentalist. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Surface chemical reaction; Low index single crystal surfaces; Nickel; Methyl iodide; Surface thermodynamics

1. Introduction

In a recent publication Mims et al. [1] have studied the decomposition of methyl iodide on Ni(111) surface both in presence and absence of pre-adsorbed hydrogen by a broad range of surface sensitive techniques. In their studies it has been observed that the dissociatively adsorbed methyl iodide either alone or co-adsorbed with hydrogen desorbs as methane at a temperature of 250 K in the course of temperature programmed desorption (TPD)studies. On the surface partially covered by pre-adsorbed hydrogen, methyl iodide undergoes decomposition to yield methane as a TPD peak at 150 K. Isotopic studies, CH_3I/D_2, revealed only CH_3D with no further isotopic scrambling. Adsorbed CH_3, I and H entities were also detected on the surface by spectroscopic methods and crowding the surface resulted in the enhancement of the adsorption peak at 150 K. The origins of the TPD peaks of methane at 150 and 250 K were traced to the reaction of so-called ''hot'' or unaccommodated surface methyl groups with

* Corresponding author. Tel.: +98-6005718; fax: +98-21-6012983.

E-mail address: gobal@ch.sharif.ac.ir (F. Gobal).

1381-1169/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(99)00345-3

adsorbed hydrogen and conventionally adsorbed (accommodated) methyl groups with adsorbed hydrogen, respectively. The ''hot'' methyl groups are meant to be those more energized than the adsorbed ones. The presence of such species is claimed to rely on the crowdedness of the surface caused by the pre-adsorbed hydrogen which presents the dominance of the access of methyl groups to lower energy surface sites. In the mentioned work no estimation of the energetics, heats of adsorption, activation energies of desorption or/and surface reactions, were made.

The purpose of the present work is to propose a model for the ''hot'' methyl species and apply the method of bond order conservation–Morse potential (BOC–MP) analysis [2] to estimate the energetics of the processes and to account for the observed TPD pattern. These authors have successfully applied the method in a number of cases [3–5] where good agreements between the calculated and experimental findings have been observed.

2. Method

In the method of BOC–MP the total bond order between the adsorbate and its underlying adsorbent atom(s) is conserved and the bond energy is assumed to follow the Morse potential model. The optimization of the energy of the adsorbed ensemble, adsorbate and its underlying surface atom(s), is achieved by a variational method [2]. The details of calculations can be found in the original literature [2,6,7]. The resulting equations used in this work for the calculations of the heats of adsorptions are given below without going into the details of derivations. Firstly, the heat of atomic adsorption of A on an n-fold surface site forming M_n–A is

$$Q_A = Q_{0A}(2 - 1/n) \tag{1}$$

where Q_{0A} is the two center bond energy. For a mono-coordinated(η^1) admolecule AB with A end down, M–A–B, three cases have been distinguished. If AB is strongly bonded onto the surface and retains its localized unpaired electron as in the case of adsorption of free radicals, one has

$$Q_{AB} = Q_A^2/(Q_A + D_{AB}) \tag{2}$$

where D_{AB} is the gas phase bond dissociation energy of AB. On the other hand if AB is weekly bonded onto the surface as in the case of the adsorption of closed shell molecules, one arrives at

$$Q_{AB} = Q_{0A}^2/(Q_{0A} + D_{AB}). \tag{3}$$

In the intermediate situation the average of the above values is employed

$$Q_{AB} = 0.5\left\{\left[Q_A^2/(Q_A + D_{AB})\right] + \left[Q_{0A}^2/(Q_{0A} + D_{AB})\right]\right\}. \tag{4}$$

So far as kinetics of the processes are concerned, the activation energies of adsorptions, surface reactions and desorptions can also be related to the Q and D values [2]. The activation energy of the dissociation of AB impinging on the surface is given by

$$\Delta E^*_{AB,g} = 0.5\left[D_{AB} + (Q_A Q_B)/(Q_A + Q_B) - Q_{AB} - Q_A - Q_B\right] \tag{5}$$

while the dissociation of the adsorbed AB species occurs with the activation energy of

$$\Delta E^*_{AB,s} = 0.5\left[D_{AB} + (Q_A Q_B)/(Q_A + Q_B) + Q_{AB} - Q_A - Q_B\right]. \tag{6}$$

Concerning the recombination of chemisorbed A and B entities, the activation energy of the desorptive recombination is

$$\Delta E_r = \Delta E_f - \Delta H \tag{7}$$

where ΔE_f is either $\Delta E^*_{AB,g}$ or $\Delta E^*_{AB,s}$ and ΔH, the enthalpy change in the reaction is obtained from

$$\Delta H = -\Sigma\left[(Q + D)_{P_i} - (Q + D)_{R_i}\right] \tag{8}$$

Table 1
Total bond energy in the gas phase (D) and heat of adsorption (Q) (kcal/mol)

Species	D[a]	Q, Ni(111)	Q, Ni(100)	Q, Ni(110)
H	–	63	66	63
C	–	171	179	171
I	–	65	68	65
CH_3I	358	15	15	15
CH_4	398	6	6	6
CH_3 (n-fold)	293	48	50	48
$CH_3^{\#}$(bridge)	293	43	43	43
$CH_3^{\#}$(on-top)	293	29	29	29

[a]Ref. [1].

where P_i and R_i refers to the products and reactants, respectively. The details of the derivations can be found in the original literature [6,7].

3. Results and discussion

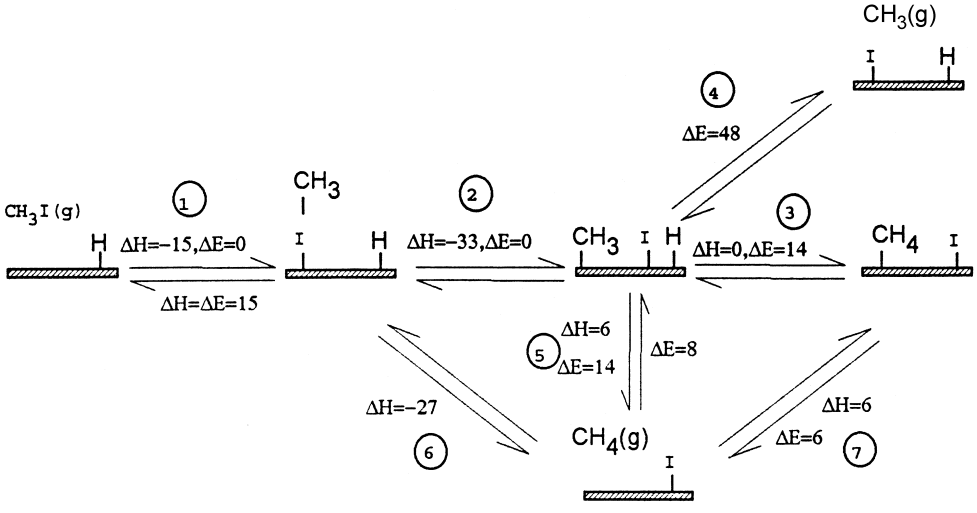
Table 1 presents the values of Q's calculated on the basis of Eqs. (2)–(4) for all types of surface species presumably involved in the reactions under consideration along with the gas phase bond energies, D's. Q's for atomic species, C, H and I are taken from the literature [1,7,8]. Enthalpy changes in the reactions are calculated using Eq. (8) and the results are presented on Schemes 1–3. Scheme 1 considers the adsorption in 3-fold hollow sites of Ni(111) surface where methyl iodide is favorably adsorbed, $\Delta H_{ads} = -15$ kcal/mol, and the process requires no activation energy. ΔG of this process was worked out using this value and ΔS given by

$$\Delta S = -R\left\{18.1 + \ln\left[(T/300)^{5/2}(m/28)^{3/2}\right]\right\} \quad (9)$$

where $T = 150$ K and m is the molecular weight of methyl iodide [9,10] and was found to be ca. -10 kcal/mol.

3.1. Reaction on 3-fold sites

The adsorbate, CH_3I, residing on a 3-fold site subsequently dissociates to adsorbed methyl group and iodine, step (2). The desorption of methyl radicals into the gas phase, step (4), requires 48 kcal/mol ($\Delta E > 0$) which is a prohibitively large value and this process is expected not to occur, which is in perfect agreement with the experimental findings [1]. On the other hand the reaction of adsorbed methyl and hydrogen to form gaseous methane, step (5), requires an activation energy of ca. 14 kcal/mol and is likely to correspond to the TPD peak of methane appearing at 250 K.



Scheme 1. The mechanism of CH_3–I bond scission and methane formation on Ni(111) with CH_3 on 3-fold site, the activation energies and the enthalpy changes are in kcal/mol.

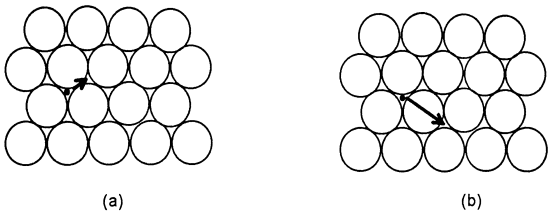


Fig. 1. The path of movement for mobile CH_3 from bridge (a) and on-top sites (b) on Ni(111).

3.2. Reaction of the ''hot'' methyl group

In order to account for the low temperature TPD peak of methane appearing at 150 K where the contribution of ''hot methyl groups'' has been proposed, we assume a mobile two dimensional gaseous $CH_3^{\#}$ intermediate with stability somewhere between the gaseous and adsorbed (on 3-fold site) methyl species. Furthermore, this species is assumed to be the result of the movements of methyl groups via

n-fold site → m-fold site → n-fold site

route. The activation energy for atomic surface diffusion [11] is

$$\Delta E_{\text{dif.}} = Q_n - Q_m \tag{10}$$

where in the present case n is 3 and refers to the 3-fold site and m is either 2 or 0 depending on that the surface species traverses via bridge or on-top sites, Fig. 1a and b, respectively. We assume the surface CH_3 acting like a quasi-atomic species which is fairly justified on account of the lack of the interaction of the methyl hydrogens with the surface signified by the absence of isotopic scrambling. The heat of adsorption of $CH_3^{\#}$ is thus given by

$$Q_{\text{2-dim.gas}} = Q_3 - \Delta E \tag{11}$$

which takes the form of

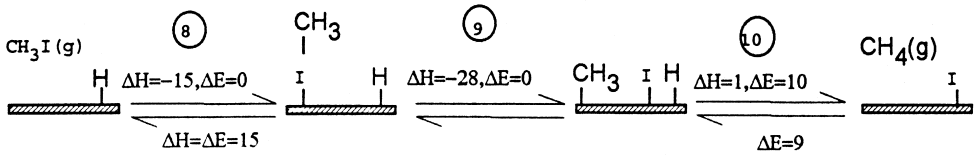
$$Q_{\text{2-dim.gas}} = Q_2 \tag{12}$$

or

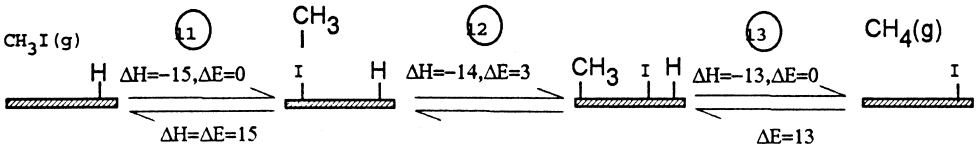
$$Q_{\text{2-dim.gas}} = Q_0 \tag{13}$$

if its mobility is achieved by passing over the bridge or on top sites, respectively.

Schemes 2 and 3 present the energetics of the formation of the two dimensional mobile surface gas, $CH_3^{\#}$, and its subsequent conversion to gaseous methane. Both routes, via bridge and on-top sites, are favoured. The latter route requires smaller activation energy and the cleavage of C—I bond with the activation energy of only 3 kcal/mol seems likely to account for the observed TPD peak at 150 K. The process of the recombination of adsorbed hydrogen and $CH_3^{\#}$, step (13), occurs with no activation energy. It is interesting to notice that the activation energy for surface mobility which is nearly 19 kcal/mol is largely provided by the dissociation of adsorbed methyl iodide to surface methyl and iodine, the latter residing on 3-fold sites. It should be emphasized that the adsorption, highly likely on the on-top position, of methyl radical formed in the gas phase onto the fully hydrogen covered surface does not give rise to the appearance of the methane TPD peak at 150 K pointing to the importance of the precursor and its mobility. The total proposed reactions paths are presented in Scheme 4.

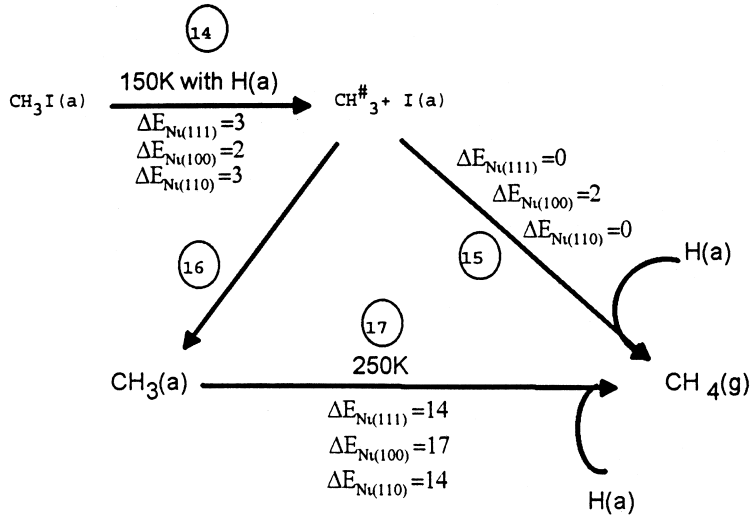


Scheme 2. The mechanism of CH_3—I bond scission and methane formation on Ni(111) with mobile CH_3 on 3-fold → bridge → 3-fold sites, the activation energies and the enthalpy changes are in kcal/mol.



Scheme 3. The mechanism of CH_3–I bond scission and methane formation on Ni(111) with mobile CH_3 on 3-fold → on top → 3-fold sites, the activation energies and the enthalpy changes are in kcal/mol.

The connection between our BOC–MP based results and the previously reported TPD measurements [1] can be elaborated further. In Fig. 1(b) of this reference two peaks have been reported in the TPD pattern. The one at 150 K is due to the reaction of mobile methyl group with hydrogen, Scheme 3, which occurs with an activation energy (ΔE) of 3 kcal/mol. Obviously, the activation energy is that of the dissociation of adsorbed methyl iodide while the surface reaction of adsorbed methyl and hydrogen species is not activated. The second peak which is at 240 K is due to the formation of methane from the reaction of methyl species adsorbed on the 3-fold sites with the hydrogen, step (5) or (17), which occurs with an activation energy of 14 kcal/mol. Fig. 2(a) of Ref. [1] shows two TPD peaks for the desorption of methyl iodide. The first peak at 135 K is due to the desorption of the physisorbed methyl iodide and occurs with the activation energy comparable to its heat of condensation. The second peak at 150 K is due to the desorption of methyl iodide. According to our calculations this process at low surface coverage requires an activation energy of 15 kcal/mol (the reverse of step (1)). At higher coverages, however, ΔE decreases and methyl iodide can leave the surface more easily at the temperature as low as 150 K. This pattern of changes is also in accord with the BOC–MP calculations we have previously exercised [3]. In Fig. 4 of Ref. [1] which is similar to Fig. 2(a), the influences of the increasing of coverages are presented. The only additional significant point is the shift of the α-CH_4 desorption peak from 170 to 150 K due



Scheme 4. Presentation of the entire reaction paths, with CH_3(a) on *n*-fold site and mobile (''hot'') $CH_3^{\#}$ traversing via *n*-fold → on top → *n*-fold sites, activation energies are in kcal/mol.

to the increasing of coverages which is also predicted by BOC–MP based calculations [3,12]. The profile of the desorption of methane from Ni(111) surface looks the same in all studies and appears at 150 K. This points to the fact that the combination of H and CH_3 is not the rate determining step in α-CH_4 formation. This is confirmed by the BOC–MP calculation which predicts zero activation energy for this step (step (13) of Scheme 3) and assumes step (12) with the activation energy of 3 kcal/mol to be the rate determining step.

To further amplify the findings, the BOC–MP results of the analysis of reaction

$$CH_4(a) \rightarrow CH_3(a) + H(a) \qquad (14)$$

presented in Scheme 1 (reverse of step (3)) were compared with the literature. The activation energy of this process calculated on the basis of BOC–MP method is 14 kcal/mol. The predicted values calculated by ASED-MO (atom superposition and electron delocalization molecular orbital) and ab initio valence orbital configuration interaction (multiple parent) methods are 15 and 17 kcal/mol, respectively [13,14] and the experimentally determined value is 13 kcal/mol [15]. It is clear that the result of BOC–MP analysis is in good agreement with the results obtained by more sophisticated and detailed methods as well as with the experimental findings [13–15]. Also, the method of BOC–MP predicted that the enthalpy of the mentioned process (reverse of step (3)) to be nearly zero, which is again in agreement with the previous reports by other researchers [14].

To emphasize the prediction capabilities of the method, this process was examined on Ni(100) and Ni(110) surfaces. The heats of adsorptions for the possible surface species were calculated by the method of BOC–MP and are presented in Table 1. ΔEs are presented on Scheme 4. The reaction of methyl iodide on Ni(100) surface has been experimentally studied [16] and it has been found that in the absence of pre-adsorbed hydrogen, methane desorbs at 220 K while in the presence of pre-adsorbed hydrogen, methane desorption forms two distinct peaks at 150 and 220 K. Our BOC–MP calculations show that ΔE of the formation of methane from the hot methyl species, step (15), and from the methyl species adsorbed on four fold sites, step (17), are 2 and 17 kcal/mol, respectively. The experimental ΔE of the cleavage of C–I bond, step (14), on Ni(100) is 3.5 kcal/mol [17] and is in fair agreement with the BOC–MP based value of 2 kcal/mol. Also, according to BOC–MP calculations the activation energies of C–I cleavage, step (14), and the formation of α-CH_4, step (15), are both 2 kcal/mol and both processes should occur at the same temperature, which is in agreement with the experimental findings [17]. No experimental studies have been reported in the literature concerning the hydrogenolysis of methyl iodide on Ni(110) surface. We have worked out ΔEs for all steps of the reaction of methyl iodide on Ni(110) surface previously covered by hydrogen. The results are presented in Scheme 4. Ni(110) behaves similarly to Ni(111) in so far as the formation of methane is concerned. It is expected that the hydrogenolysis of methyl iodide on Ni(110) surface under the TPD regime would also give rise to two methane peaks, one at around 150 K and the other around 240 K. The confirmation of these findings are left to the experimentalists.

4. Conclusion

On the basis of the above calculations the involvement of more energized ''hot'' surface species in the course of the decomposition reaction of methyl iodide on Ni(111) surface, previously largely covered by adsorbed hydrogen, is justified. The Scheme 3 shows that the rate limiting step of the process which gives rise to the peak at 150 K is the CH_3–I bond scission, step (12), ($\Delta E = 3$ kcal/mol) and the H-atom transfer in α-methane formation, step (13), is not the rate limiting step ($\Delta E = 0$). This is in perfect agreement with the experimental finding

where in all TPD experiments, α-methane peaks appear at the same temperature and are of similar shapes. Also, the power of this astonishingly simple and successful theoretical method in deriving the energetics of the catalytic processes is signified.

References

[1] M.E. Castro, J.G. Chen, R.B. Hall, C.A. Mims, J. Phys. Chem. B 101 (1997) 4060.
[2] E. Shustorovich, Adv. Catal. 37 (1990) 101.
[3] F. Gobal, S. Azizian, Langmuir 13 (1997) 5999.
[4] F. Gobal, S. Azizian, J. Chem. Res. (1997) 324.
[5] F. Gobal, S. Azizian, J. Mol. Catal. A: Chem. 136 (1998) 169.
[6] E. Shustorovich, Surf. Sci. 163 (1985) L730.
[7] E. Shustorovich, Surf. Sci. 181 (1987) L205.
[8] E. Shustorovich, E.T. Bell, Surf. Sci. 248 (1991) 359.
[9] T.L. Hill, An Introduction to Statistical Thermodynamics, Addison-Wesley, Menlo Park, CA, 1960.
[10] J.B. Benziger, Appl. Surf. Sci. 6 (1980) 105.
[11] E. Shustorovich, J. Am. Chem. Soc. 106 (1984) 6479.
[12] E. Shustorovich, Surf. Sci. 163 (1985) L645–L654.
[13] A.B. Anderson, J.J. Maloney, J. Phys. Chem. 92 (1988) 809.
[14] H. Yang, J.L. Whitten, J. Chem. Phys. 96 (1992) 5529.
[15] T.P. Beebe Jr., D.W. Goodman, B.D. Kay, J.T. Yates Jr., J. Chem. Phys. 87 (1987) 2305.
[16] S. Tjandra, F. Zaera, J. Am. Chem. Soc. 114 (1992) 10645.
[17] S. Tjandra, F. Zaera, J. Vac. Sci. Technol., A 10 (1992) 404.