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The Enthalpy Changes in the Course of Ethylamine Decomposition on a Ni(111) Surface†

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The BOC-MP method is capable of calculating the enthalpies of various adsorbates in the catalytic decomposition of ethylamine on Ni(111) with results in good agreement with the experiments and superior to the extended Hückel approximation predictions.

Surface-sensitive spectroscopic methods are capable of providing extensive information regarding the structure of observed intermediates and reaction mechanisms. However, little information about the energies involved in these processes is provided. The present study applies the method of bond order conservation–Morse potential analysis[1] (BOC-MP) to investigate the heat of adsorption of ethylamine and the enthalpies of the possible intermediates in the decomposition of this species to acetonitrile and hydrogen on a Ni(111) surface. This process has been studied in some detail by Somorjai *et al.*[2] where the methods of temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were employed. It has been concluded that the dehydrogenation starts by an α-H—C cleavage, and the subsequent dehydrogenation of the ensuing $MeCNH_2$ (**2**) and MeCNH (**4**) species gives rise to MeCN. On the basis of the TPD and HREELS results, the enthalpies of all the species were calculated (Table 1). In a further endeavour, Somorjai *et al.*[3] attempted to calculate the enthalpies by the extended Hückel method with the inclusion of a repulsive correction[4] for various pairs of adsorbate atoms but ignoring the repulsion between the metal and adsorbate (Table 1). Although the treatment reproduces the trend, it largely over-estimates the enthalpies.

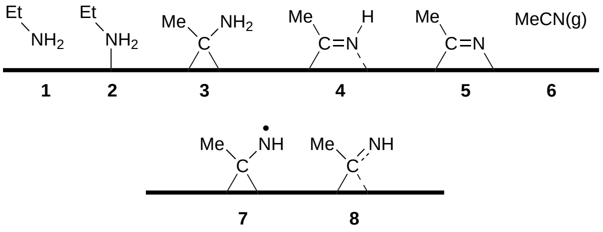

Fig. 1

Table 1 Enthalpies of the gas phase (g) and adsorbed (a) species

Species	ΔH (BOC-MP)/ eV	ΔH (exp.)/ eV[a]	ΔH (ext. Hückel)/ eV[a]
1	0.00	0.00	0.00
2	−0.86	−0.78	−1.71
3+2H(a)	−1.12	−1.04	−2.00
4+3H(a)	0.66 (−1.86)	−1.65[b]	−4.08
5+4H(a)	−1.85	−1.72	−4.79
6+4H(a)	−1.03	−0.82	−2.37
6+2H(a)+H_2(g)	−0.08	0.17	−0.53
6+2H_2(g)	0.87	1.17	1.31

[a]Ref. 3. [b]Calculated on the basis of experimental bond energies.[2]

We have employed the BOC-MP method to calculate the heats of adsorption of the surface species proposed by Somorjai.[2,3] Table 2 shows the values of the gas phase bond energies (D) and the heats of atomic and molecular chemisorption (Q) calculated using the equations in the appendix of ref. 5 neglecting the destabilizing/stabilizing effects of the changes of the surface coverages of the adsorbates.[6] From these results and using eqn. (1) the enthalpies were calculated and the results are presented in Table 1. In eqn. (1), P and R refer to the products and the reactant [$MeCH_2NH_2$(g)] respectively.

$$\Delta H = -[\Sigma(Q+D)_P - \Sigma(Q+D)_R] \qquad (1)$$

The agreement with the experimental results is very good and the deviations never exceed 0.3 eV except for the case of the acimidoyl group **4** where the BOC-MP analysis gives a highly under-estimated value. It must be emphasized that the reported enthalpy of **4** is not an experimental finding and is calculated on the basis of bond energies. On the basis of the BOC-MP analysis it seems that **4** is unlikely to be the intermediate. This intermediate has been proposed[2] on the basis of the HREELS peaks at 1350 and 3300 cm^{-1} assigned to the C=N—H structure adsorbed on the surface *via* C and N and by comparison with the corresponding organometallic compound.[2] Although this structure with the C=N 'softened' by adsorption may be present on the surface, it is probably not the one taking part in the reactions and desorbing as MeCN in the course of a TPD run.

It seems that the interaction with the surface which relaxes the double bond should strengthen the N—H bond and shift it to higher wavenumbers, yet the reverse has been observed. Assuming structure **7**, the enthalpy of adsorption was calculated (Table 1).

Considering the structure **8** where the C—N bond has been somewhat strengthened, the enthalpy is around −1.41 eV which is far better than the Hückel value. In this structure the C—N bond order is certainly higher than that in **7** and could possess the stretching frequency around 1350 cm^{-1}, midway between that of C—N (*ca.* 1100 cm^{-1}) and that of C=N (*ca.* 1650 cm^{-1}). In fact, owing to the exothermicity of the surface reactions, the enthalpy of this species must lie in

Table 2 Heat of adsorption (Q) and total bond energies in the gas phase (D) and chemisorbed state ($Q+D$) on Ni(111)

Species	D/eV	Q/eV	$Q+D$/eV
C	—	7.42	7.42
N	—	5.85	5.85
H	—	2.73	2.73
2	35.43	0.86	36.29
3	27.36	3.73	31.09
4	25.93	0.65	26.58
5	25.54	0.82	26.36
6	25.54	—	25.54
7	25.93	3.17	29.10
8	23.93	2.73	28.66
H_2(a)	4.51	0.30	4.81
H_2(g)	4.51	—	4.51

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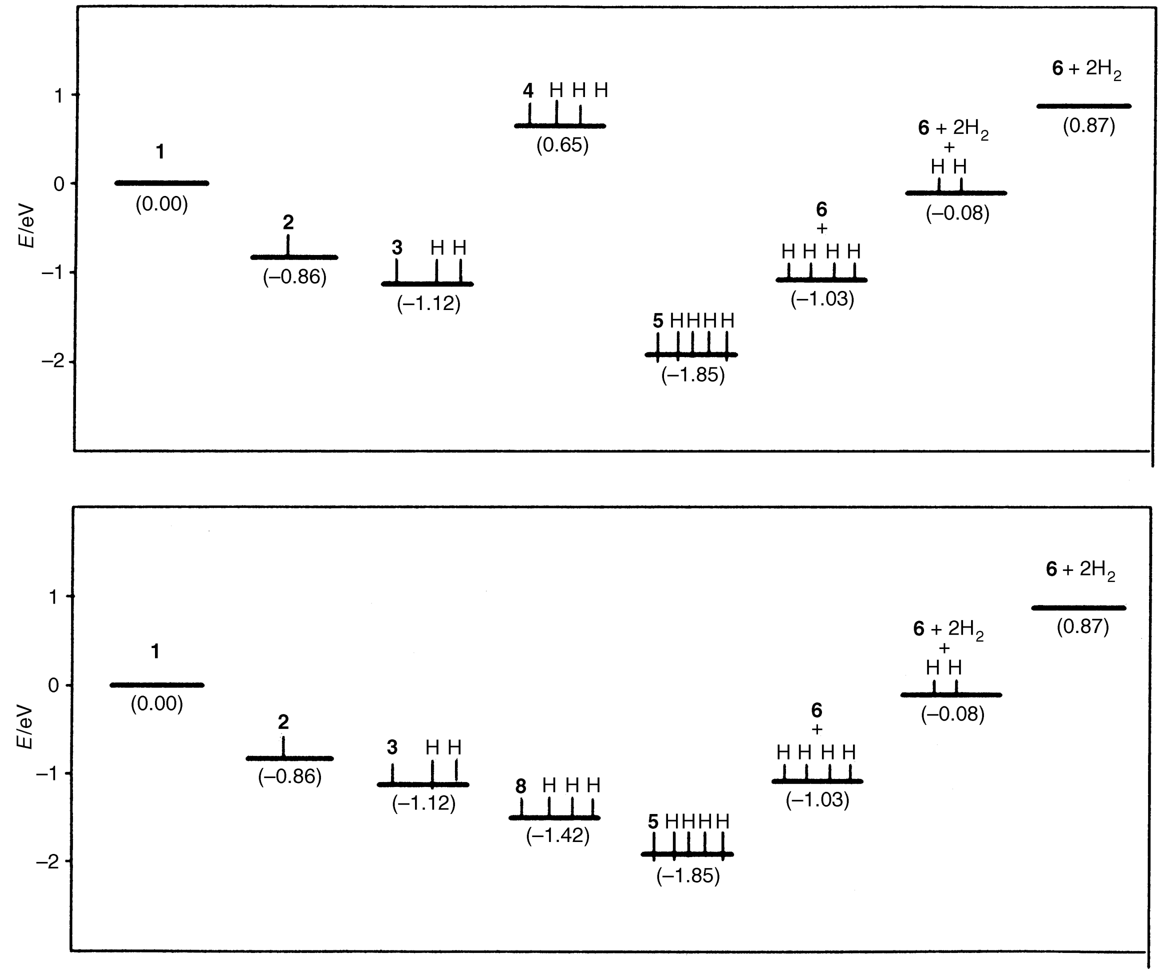

Fig. 2 Enthalpies of the surface reactions

Table 3 Heat of adsorption (*Q*)

Species	*Q* (BOC-MP)/eV	*Q* (exp.)/eV	*Q* (Hückel)/eV
$MeCH_2NH_2$ **2**	0.86	*ca.* 0.8	1.71
MeCN-η^2	0.82	*ca.* 0.9	2.42
MeCH-η^1	0.95	—	2.87

the range −1.12 to −1.85 eV (Fig. 2). The calculated value for structure **8** is well within this range. Table 3 compares the heat of adsorptions of ethylamine and acetonitrile in both η^1- and η^2-coordinations where again the values obtained by the BOC-MP method are very close to the experimental values and the method is by far superior to the extended Hückel approximation. We believe that the good agreement between the BOC-MP-based calculation and the experimental findings stems from the use of fairly accurate atomic heats of adsorption and dissociation energies used in the calculations.

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