SHORT PAPER

J. Chem. Research (S),
2000, 520–521

A study of the mechanism of chlorine adsorption–desorption on a Pt(111) surface: a UBI–QEP approach[†]

S. Azizian and F. Gobal*

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

UBI–QEP based study of the desorption of both atomic and molecular chlorine from Pt(111) surface revealed that in both cases the precursor, atomic chlorine, originates from the three-fold sites and migrate to the on-top positions where desorptions occur.

Schennach and Bechtold[1] have studied the interaction of chlorine with the most stable low index Pt(111) and Pt(110) surfaces employing the methods of low energy electron diffraction (LEED) and temperature programmed desorption (TPD). Adsorption of chlorine atoms yields a (3×3) structure containing five chlorine atoms. The desorption as both Cl_2 and Cl have been reported in well separated desorption temperature ranges. Activation energies and site non-specificities of the desorption have been reported. The purpose of the present work is to shed light on the mechanism of the desorptions of these species by calculating the energetics of the surface processes by the method of unity bond index-quadratic exponential potential, UBI–QEP.[2] We have successfully applied the method to study a number of catalytic processes.[3–5]

The UBI–QEP method employs the most general two body interaction potentials. The potential variable, named bond index, is a general exponential function of the two–centre bond distance. The bond indices of interacting atoms are assumed to be conserved at unity (up to the dissociation point). The UBI–QEP method allows one to calculate heats of adsorptions and reaction activation barriers. The details of calculations can be found in the original literature.[2] The resulting equations used in this work are given below without going into the details of the derivations.

Firstly, the heat of atomic adsorption of A on an *n*-fold surface site forming M–A is

$$Q_{nA} = Q_{0A}\,(2 - 1/n) \qquad (1)$$

Where Q_{0A} is the two-centre bond energy. For a homonuclear admolecule A_2 parallel to the surface one has

$$Q_{A2} = 9Q^2_{0A} \,/\, (3Q_{0A} + 16D_{A2}) \qquad (2)$$

Where D_{A2} is the gas phase bond dissociation energy of A_2. The activation energy of the dissociation of AB impinging on the surface is given by

$$\Delta E_{AB,g} = 0.5[D_{AB} + (Q_A Q_B) \,/\, (Q_A + Q_B) - Q_{AB} - Q_A - Q_B] \qquad (3)$$

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

$$\Delta E_{AB,s} = 0.5[\,D_{AB} + (Q_A Q_B) \,/\, (Q_A + Q_B\,) + Q_{AB} - Q_A - Q_B] \qquad (4)$$

the activation energy of the reverse reaction is

$$\Delta E_r = \Delta E_f - \Delta H \qquad (5)$$

where ΔE_f is either $\Delta E_{AB,g}$ or $\Delta E_{AB,s}$ and ΔH, the enthalpy changes in the reaction is obtained from

$$\Delta H = \Sigma\,[(Q + D)_{Pi} - (Q + D)_{Ri}] \qquad (6)$$

with P_i and R_i refer to the products and reactants respectively.

The experimental heat of adsorption (Q_{nA}) of chlorine on Pt(111) is 94 kcal/mol.[6] This species occupies three-fold sites in accordance with the LEED results. Using the atomic heat of adsorption of chlorine in the UBI–QEP scheme, the heat of adsorption of chlorine on the on-top position is found to be Q_{0A} = 56 kcal/mol. These values will be employed in the calculation carried out throughout this work.

Table1 summarizes the activation energies for both the forward and reverse reactions (ΔE_f, ΔE_r) as well as the enthalpy changes of all the expected process of chlorine on the Pt(111) surface as calculated by the method of UBI-QEP. The calculations are carried out at 6 levels of the surface coverages ranging from $\theta = 0$ to 1. The details of the calculations have been explained previously.[2,7,8]

At $\theta = 0$, Cl_2 adsorbs molecularly (reaction (1)) with no activation energy and with the heat of adsorption of –23 kcal/mol. This species may further dissociate to atomic chlorine on the on-top (reaction (2)), bridge (reaction (3)) and 3-fold (reaction (4)) positions, all with no activation energies but the last is accompanied by a substantially larger, –108 kcal/mol, enthalpy change that points to the stability of the adsorbed species. Also, gaseous chlorine can directly dissociate to form the mentioned species (reactions (5)–(7)) with no activation energies but accompanied by the enthalpy changes, which for reaction (7) amounts to –131 kcal/mol making it the most favoured. These results are in accord with the LEED results which at 300K show a (3×3) cell consisting of five chlorine atoms.[1]

Comparing the experimental activation energy of the desorption of atomic chlorine from the Pt(111) surface[1] with those of Table 1 reveals the correspondence with that of reaction 10 which is the desorption of chlorine from the on-top positions. It seems to us that upon increasing temperature, chlorine atoms migrate from the 3-fold sites to the on-top positions prior to desorption. A part of the surface chlorine atoms desorb as Cl_2 and the desorption activation energies of this process, E_2, and that of the desorption of atomic chlorine, E_1, follows $2E_1 - E_2 = 59 \pm 2$ kcal/mol as reported by Schennach *et al*.[1] Having calculated the E_1 values at different coverages, table 1 reaction 10, E_2 values have been derived at the coverages of 0, 2/5, 3/7, 1/2, 3/5 and 1 and are 53, 43, 37, 35, 19, 3 (±2) kcal/mol respectively. Comparing this sequence with the data presented in Table 1 for the processes of the desorption of $Cl_{2(g)}$, good correspondence with the activation energies of the reverse of reaction (5) have been observed. On this basis, it seems that chlorine atoms migrate from the 3-fold sites to the on-top position and desorb as molecular chlorine.

---

* To receive any correspondence. E-mail: gobal@ch.sharif.ac.ir

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Activation energies of the forward and reverse reactions and the enthalpy changes at various surface coverages

	θ = 0			θ = 2/5			θ = 3/7			θ = 1/2			θ = 3/5			θ = 1		
	ΔE_f	ΔH	ΔE_r	ΔE_f	ΔH	ΔE_r	ΔE_f	ΔH	ΔE_r	ΔE_f	ΔH	ΔE_r	ΔE_f	ΔH	ΔE_r	ΔE_f	ΔH	ΔE_r
(1) $Cl_{2(g)} \Leftrightarrow Cl_{2(s)}$	0	–23	23	0	–21	21	0	–20	20	0	–19	19	0	–16	16	0	–13	13
(2) $Cl_{2(s)} \Leftrightarrow 2Cl^*$	0	–32	32	0	–25	25	3	–18	21	3	–17	20	7	–6	13	12	8	4
(3) $Cl_{2(s)} \Leftrightarrow 2Cl_{(b)}$	0	–88	88	0	–76	76	0	–66	66	0	–64	64	0	–45	45	0	–23	23
(4) $Cl_{2(s)} \Leftrightarrow 2Cl_{(3f)}$	0	–108	108	0	–94	94	0	–83	83	0	–81	81	0	–59	59	0	–34	34
(5) $Cl_{2(g)} \Leftrightarrow 2Cl^*$	0	–55	55	0	–46	46	0	–38	38	0	–36	36	0	–22	22	0	–5	5
(6) $Cl_{2(g)} \Leftrightarrow 2Cl_{(b)}$	0	–111	111	0	–97	97	0	–86	86	0	–83	83	0	–61	61	0	–36	36
(7) $Cl_{2(g)} \Leftrightarrow 2Cl_{(3f)}$	0	–131	131	0	–115	115	0	–103	103	0	–100	100	0	–75	75	0	–47	47
(8) $Cl_{(b)} \Leftrightarrow Cl^*$	28	28	0	26	26	0	24	24	0	23	23	0	20	20	0	16	16	0
(9) $Cl_{(3f)} \Leftrightarrow Cl^*$	38	38	0	35	35	0	32	32	0	32	32	0	27	27	0	21	21	0
(10) $Cl^* \Leftrightarrow Cl_{(g)}$	56	–56	0	51	–51	0	48	–48	0	47	–47	0	39	–39	0	31	–31	0
(11) $Cl_{(b)} \Leftrightarrow Cl_{(g)}$	84	–84	0	77	–77	0	72	–72	0	70	–70	0	59	–59	0	47	–47	0
(12) $Cl_{(3f)} \Leftrightarrow Cl_{(g)}$	94	–94	0	86	–86	0	80	–80	0	78	–78	0	66	–66	0	52	–52	0

Cl^*: chlorine atom on the on-top position.
$Cl_{(b)}$: chlorine atom on the bridge position.
$I_{(3f)}$: chlorine atom on the three-fold position.

This mechanism is in accord with the reported changes of the LEED pattern where the (3×3) structure converts to a disordered structure at above 500K and also the increased chlorine adsorption at this temperature range.[1] These results points to the fact that the desorbing species are fairly mobile at elevated temperature in accordance with our proposed mechanism. It has been reported[1] that rate of desorption of chlorine atoms which is expected to be first order does not increase linearly with pressure (surface coverage). This finding is nicely accounted for by the application of the UBI-QEP method via considering the fall of the activation energy of desorption due to the repulsive interaction[2,7] of the surface species upon increasing surface coverage, reaction (10) of Table 1.

Conclusions

On the basis of this study the following conclusions are reached

(i) On the Pt(111) surface, atomic chlorine occupy 3-fold sites.

(ii) Desorptions of both atomic and molecular chlorine occur from the on-top sites.

(iii) High chlorine coverage results in lowering of the activation energies of desorption due to the repulsive interaction of the surface species.

Received 25 June 2000; accepted 21 October 2000
Paper 00/403

References

1 R. Schennach and E. Bechtold, *Surface Science*, 1997, **380**, 9.
2 E. Shustorovich and H. Sellers, *Surface Science Reports*, 1998, **31**, 1.
3 F. Gobal and S. Azizian, *J. Chem. Research(s)*, 1997, 324.
4 F. Gobal and S. Azizian *J. Mol. Catal. A: Chemical*, 1998, **136**, 164.
5 S. Azizian and F. Gobal, *J. Mol. Catal. A: Chemical*, 2000, **153**, 191.
6 M. P. Kiskinova, *Surface Science Reports*, 1988, **8**, 359.
7 E. Shustorovich, *Surface Science*, 1985, **163**, L645.
8 F. Gobal and S. Azizian, *Langmuir*, 1997, **13**, 5999.