

# Notes

## Chemisorption of Nitrous Oxide on Transition Metal Surfaces—Bond Energy Bond Order Model Calculation

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Using the Bond Energy Bond Order (BEBO) model calculation for the chemisorption of nitrous oxide on various transition metals, it has been shown that there is no stable molecularly adsorbed state on the surface and the molecules undergo rapid dissociation on most of these metal surfaces. The predicted activity pattern in terms of the heat of adsorption for various transition metals is in good agreement with the pattern observed experimentally.

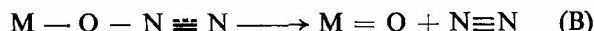
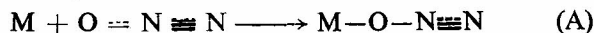
AMONG the theoretical methods available for the study of adsorption of gaseous molecules on solid surfaces, the Bond Energy Bond Order (BEBO) method<sup>1-4</sup> has been increasingly used due to its simplicity and its ability to give results comparable to those obtained by semi-empirical quantum mechanical calculations. In this note the chemisorption of nitrous oxide on various transition metals has been treated within the framework of the BEBO model, with a view to predicting the activity order of the transition metals towards adsorption and decomposition of nitrous oxide. The adsorption of nitrous oxide on platinum metal alone has been studied by Weinberg<sup>5</sup>.

In BEBO model calculation of Weinberg<sup>5</sup>, nitrous oxide molecule is considered to approach the metal surface through nitrogen and the results predict the reaction to be endothermic and its heat of chemisorption is unrealistic. In the present calculations, it has been assumed that nitrous oxide approaches and gets adsorbed on the metal through the oxygen atom, which seems more probable.

The molecular orbital diagram of nitrous oxide shows that  $2\sigma_g^+$  and doubly degenerate  $1\pi_a$  molecular orbitals are used to form  $O=N\equiv N$  bonds. Further there are three lone pairs of electrons namely,  $2\sigma_a^+$  on oxygen and doubly degenerate  $1\pi_d$  on terminal nitrogen atom. It is presumed that the  $2\sigma_a^+$  electrons on oxygen are utilised for bonding with the metal surfaces.

In gaseous nitrous oxide molecule the bond order  $\eta_{O-N}$  of O-N bond is 1.5 (ref. 5) and that of N-N bond  $\eta_{N-N}$  is considered as 2.35 in order that the interaction energy  $V_{N_2O}$  calculated by step (A) and step (B) are the same at the bond order  $\eta_{M-O} = 1.0$ . As the nitrous oxide approaches the metal through oxygen atom, the  $\eta_{O-N_2}$  decreases and simultaneously

the  $\eta_{M-O}$  of forming  $\frac{1}{2}M-O$  increases. The whole process is assumed to take place in the following two steps :



The interaction energy between the gaseous molecule and the metal for the various bond order values are calculated in terms of the Born-Haber cycle.

Bond order variations considered in step (A) are :  $0 \leq \eta_{M-O} \leq 1.0$ ; and  $1.5 \geq \eta_{O-N_2} \geq 1.0$ . The energetics involved in step (A) may be written as

$$V_{N_2O} = D_{N_2O} - E_{M-ON_2} - E_{O-N_2, surf} \quad \dots (1)$$

where  $V_{N_2O}$  is the interaction energy,  $D_{N_2O}$  is the dissociation energy of the nitrous oxide<sup>6</sup>,  $E_{O-N_2, surf}$  is the energy of O-N<sub>2</sub> bond in the adsorbed state;  $E_{M-ON_2}$  is obtained from the relation

$$E_{M-ON_2} = \eta_{M-ON_2} \cdot E_{M-ON_2, surf} \quad \dots (2)$$

where  $\eta_{M-ON_2}$  is calculated in terms of O-N<sub>2</sub> bond order through the relation,

$$\eta_{M-ON_2} = \lambda(\eta^{\circ}_{O-N_2} - \eta_{O-N_2}) \quad \dots (3)$$

where  $\lambda$  is the ratio between forming bond order to loosening bond order (in this case  $\lambda = 1/0.5 = 2$ ) and  $\eta^{\circ}_{O-N_2}$  is the bond order of O-N<sub>2</sub> bond in free gaseous molecule.  $E_{M-ON_2, surf}$  is the single bond energy of M-O bond and it has been calculated and tabulated by Miyazaki<sup>4</sup> for various transition metals using parameterised Pauling-Eley equation.

$E_{O-N_2, surf}$  has been calculated<sup>5</sup> as a function of the bond orders of O-N<sub>2</sub> bond using the relation(4).

$$E_{O-N_2, surf} = -6\eta_{O-N_2}^3 + 43\eta_{O-N_2}^2 - 3\eta_{O-N_2} \quad \dots (4)$$

Thus the interaction energies have been calculated using Eq. (1) for the bond order variation of 1.5 to 1.0 for the bond O-N<sub>2</sub>. The bond order variations considered in step (B) are :  $1.0 \leq \eta_{M-O} \leq 2.0$ ;  $1.0 \geq \eta_{O-N} \geq 0.0$ ; and  $2.35 \leq \eta_{N-N} \leq 3.0$ . The energetics involved in step (B) may be written as :

$$V_{N_2O} = D_{N_2O} - E_{M-ON_2} - E_{O-N_2, surf} - E_{N-N} \dots (5)$$

$E_{N-N}$  corresponds to the increase in the bond energy of N-N bond, due to increase in its bond order from 2.35 to 3.0 in the step (B) and is calculated from the relation (6)

$$E_{N-N} = [0.65 - (\eta_{O-N} \times 6.65)]. E_{N-N}(g) \quad \dots (6)$$

where  $E_{N-N}(g)$  is the single bond energy of N-N bond in gaseous state (=38 kcal/mol).

The interaction energy between N<sub>2</sub>O and metal surface is calculated from Eq. (5) for the bond order variation from 1.0 to 0.0 for the bond O-N<sub>2</sub>.

The interaction energies calculated at various bond orders are plotted as a function of bond order of the loosening bond ( $O-N_2$ ) and the pattern is shown in Fig. 1.

The absence of any shallow in the patterns at the early stages (near  $\eta_{O-N_2} = 1$ ) reveals that there is no stable molecularly adsorbed species. The breaks in the curves indicate that there may be a metastable molecular state, which immediately undergoes further dissociation. Thus the BEBO calculation predicts that nitrous oxide molecule undergoes mostly an exothermic dissociative chemisorption on transition metals.

It has been experimentally shown<sup>7-11</sup> that the rate of decomposition of nitrous oxide on transition metal surfaces is directly proportional to the pressure of nitrous oxide. Further, it was also observed<sup>7</sup> that nitrous oxide undergoes rapid dissociative chemisorption with nitrogen evolution, leaving an oxide surface layer. These experimental observations justify the assumptions made for the model calculations.

The activity of various metals to decompose nitrous oxide as predicted by the magnitudes of heats of adsorption calculated by BEBO model is  $W > Fe \approx Ni > Pd \approx Pt \approx Ir$ . The activity predicted experimentally<sup>9-11</sup> is in the order  $Fe \approx Ni > W > Pd \approx Pt > Ir$ . Thus, the activity pattern agrees with the observed

trend with a few exceptions like W and Ir. The exceptions can be due to additional complications like : (i) simultaneous formation of nitric oxide, during adsorption of nitrous oxide on these surfaces; (ii) inhibition due to strongly adsorbed oxygen on some metals; and (iii) condensation of nitrous oxide over the surface.

These calculations suggest a trend for making further rigorous quantum mechanical calculations. However, the model requires major modifications so as to be applicable to ionic solids.

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#### Electrolytically Generated 4-(2'-Thienyl)quinazoline Radical : Decay in Dipolar Aprotic Media

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The electrolytically generated radical from 4-(2'-thienyl)quinazoline in dimethylformamide and acetonitrile solutions containing 0.1M tetrabutylammonium iodide as supporting electrolyte has been investigated by EPR spectroscopy. The various possibilities for the observed decay pattern of the radical are discussed.

THE key intermediate, 4-(2'-thienyl)quinazoline (4-TQ)<sup>1</sup>, in the preparation of 4-(2'-thienyl)quinazolinone is reduced in two one-electron steps at d.m.e. to give 3,4-dihydro-4-TQ as the final product in amphiprotic<sup>2</sup> (methanol-water mixtures) and dipolar aprotic [N,N-dimethylformamide<sup>1</sup> (DMF) and acetonitrile (AN)] media. The first step of reduction in DMF and AN solutions gives 4-TQ neutral radical, the presence of which has been confirmed by EPR experiments<sup>3</sup>. In this note, we present the EPR results for the 4-TQ radical decay in dipolar aprotic media.

The EPR spectrum of 4-TQ radical obtained at the limiting region of the first polarographic wave (at -1.300 V versus silver wire electrode) in DMF at 25°C in the presence of 0.1M tetrabutylammonium

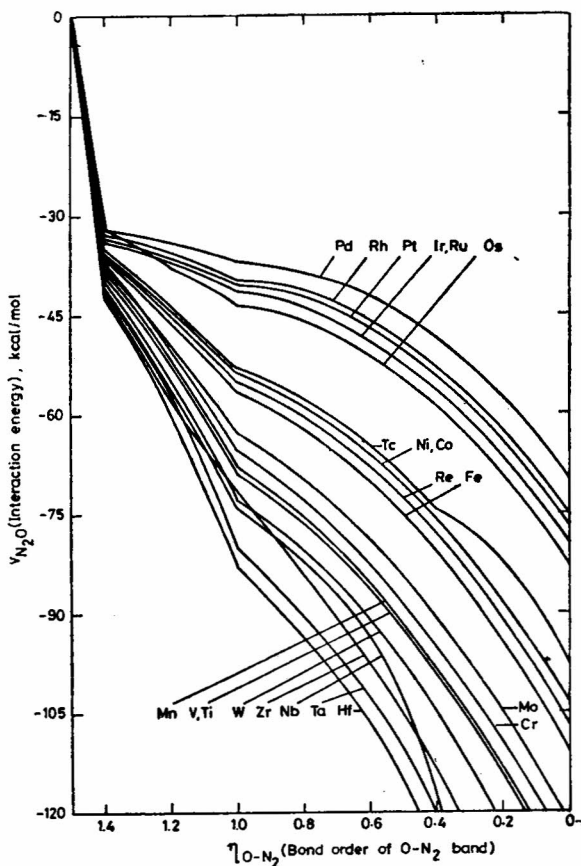


Fig. 1 — Variation of interaction energy as a function of the loosening bond order of  $N_2O$  as a result of adsorption on transition metal surfaces.