JOURNAL OF CATALYSIS 28, 459–470 (1973)

A Model Description of the Adsorption and Decomposition of Nitrous Oxide on Clean and Carbon Covered Platinum Surfaces

W. H. WEINBERG

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109

Received August 17, 1972

The bond energy bond order (BEBO) model of chemisorption has been used in conjunction with absolute rate theory (ART) in order to describe the interaction of N_2O with both clean and C covered Pt surfaces. The BEBO model allows an estimate to be made of both activation energies to, and heats of, adsorption and/or surface reactions. Combining the BEBO model with ART permits absolute magnitudes of the rates of the various elementary surface reactions which occur when N_2O interacts with Pt to be calculated *a priori*. The rate calculations are made using the experimental conditions of West and Somorjai, namely $T = 1125°K$ and an impingement flux of $\sim 10^{13}$ molecules/cm^2 sec. Under the experimental conditions cited above, the model calculations indicate the following: (a) The Pt surfaces are rather inefficient at dissociating N_2O ($\lesssim 1\%$ of the incident N_2O molecules are dissociated); (b) The fractional coverages of adsorbed N and O atoms are small, i.e., the clean Pt surface remains very nearly clean during the reaction ($\theta_N \sim 5 \times 10^{-5}$ and $\theta_O \sim 10^{-2}$); and (c) The reaction of N_2O with PtC is a direct reaction to produce NO(g) without complete energy accommodation of the NO at the surface, whereas the reaction of N_2O with clean Pt has two components to produce NO(g)—both a direct reaction of the N_2O and the desorption of an adsorbed N atom and O atom, i.e., energy accommodation of the NO at the surface is much more complete. The theoretical and experimental results show very good agreement with one another. The clear utility of the ART-BEBO model in describing numerous other elementary gas-surface reactions is an important conclusion of this work.

Introduction

An empirical model description of chemisorption and heterogeneously catalyzed surface reactions has recently been developed using features of the crystal field theory (*1*), the Engel–Brewer rules for electronic and geometric structure of transition metals and alloys (*2*, *3*), and the bond energy bond order (BEBO) correlations of gas phase spectroscopy (*4*). This model has previously been used quite successfully to describe the following gas–surface interactions: (a) the chemisorption of H_2 on (111)Pt (*5*); (b) the chemisorption of CO, O_2 and CO_2 on (111)Pt and O_2 on (111)Ni (*6*); (c) the chemisorption of O_2 on (111)Pt and a Pt surface contaminated by C (*7*); (d) the chemisorption of N_2, NO and N_2O on (111)Pt and N_2O on (111)Ni (*8*); (e) the catalytic reactions $CO + O_2$, $CO + NO$, and $H_2 + O_2$ on Pt (*9*); and (f) the hydrogenation of C_2H_4 and the nucleation of graphitic carbon on (111)Pt (*10*). A review of the BEBO model applied to chemisorption has also recently been given (*11*).

In this communication the BEBO model is applied to the interaction of N_2O with both clean and carbon covered Pt surfaces. This is a unimolecular decomposition reaction which results in the formation of either N_2 or NO in the gas phase and either an adsorbed oxygen or nitrogen atom. Cata-

lytic reactions of N_2O with both Pt=O and Pt≡N are also considered. These are the reactions which regenerate the clean catalyst surface. The BEBO model is also used to treat the chemical adsorption and desorption of both N_2 and O_2 on Pt. The use of absolute rate theory together with the BEBO model (the latter of which allows an estimate of relevant activation energies) permits a comparison among the rates of the various reactions which occur when N_2O interacts with both Pt and PtC. This system is a useful one on which to make these model calculations since West and Somorjai (*12*) have recently reported experimental molecular beam data for N_2O reactions with a clean (100)Pt surface as well as one which is covered with C.

BEBO Model and Absolute Rate Theory

The BEBO model of chemisorption and surface reactions has been described in detail previously (*5–11*). The model permits a calculation of the interaction energy when gaseous species either interact with a solid surface (chemisorption) or else interact with a previously adsorbed species (heterogeneous catalysis with Rideal-Eley kinetics). The interaction of two adsorbed species may also be described using the BEBO model (catalysis with Langmuir-Hinshelwood kinetics). When a gas molecule interacts with a clean surface, the interaction energy V may be written as

$$V = \sum_{ij} D_{ij} - \sum_{ij} E_{ij,S} - \sum_{i} E_{S-i}, \quad (1)$$

where D_{ij} is the dissociation energy of the molecular specie being adsorbed (the total bond energy in all the ij bonds of the molecule), $E_{ij,S}$ is the total energy in the ij bonds of the adsorbing molecule as it interacts with the surface S, and E_{S-i} is the total energy in the bonds formed between the surface and the adsorbing molecule. The dissociation energies D_{ij} are available from gas phase data, and values of $E_{i-j,S}$ are known as a function of bond order from BEBO correlations of molecular spectroscopy. The relationship between the energy in the S–i bond and the bond order n_{S-i} is assumed to be linear (*5–11*), i.e.,

$$E_{S-i} = E_{S-i,s} n_{S-i}, \quad (2)$$

where $E_{S-i,s}$ is the energy of the single order S–i bond. The relationship between n_{S-i} and n_{i-j} is obtained by conserving charge, that is by conserving chemical bonds. Thus, all the machinery is now available to calculate the interaction energy of a gaseous molecule with a solid surface as a function of bond order (either n_{ij} or n_{S-i}). The extension of the model to treat heterogeneous catalysis is straightforward using a generalized equation essentially equivalent to Eq. (1). The extension will become clear when the model is applied to the specific case of N_2O interactions with both clean and carbon covered Pt surfaces in the following section.

It is possible to calculate the rates of various elementary gas–surface reactions (e.g., adsorption, desorption or catalytic surface reactions) by applying the absolute rate theory using activation energies calculated using the BEBO formulation. The absolute rate theory has been used in this fashion to calculate the sticking probability of O_2 on both clean and C contaminated Pt surfaces (*7*). The theoretical results will be presented only briefly here considering the several possible types of surface reactions mentioned above.

The rate of adsorption may be written as (*7, 13, 14*)

$$R_a \simeq (1 - \theta) \frac{p}{(2\pi m k T)^{1/2}} \exp(-E_a^a/kT), \quad (3)$$

where $1 - \theta$ is the fraction of surface not covered by adsorbate; p is the gas phase partial pressure of the adsorbing molecule; m is the mass of the gaseous molecule; k is the Boltzmann constant; T is the absolute temperature; and E_a^a is the activation energy to chemisorption. Heterogeneously catalyzed surface reactions obeying Rideal-Eley kinetics where one of the reactants is adsorbed and the other is present in the gas phase may be analyzed using absolute rate theory. The reaction rate may be written as (*13, 14*)

$$R_r^{\text{R-E}} \simeq \theta \frac{p}{(2\pi mkT)^{1/2}} \exp(-E_a^{\text{R-E}}/kT), \quad (4)$$

where the coverage of the adspecies is given by θ, the impingement flux is given by $p/(2\pi mkT)^{1/2}$, and $E_a^{\text{R-E}}$ is the activation energy to chemical reaction. The rate of desorption from a surface may be written in the following way using absolute rate theory (*13, 14*)

$$R_d \simeq 10^{28}\theta_{ij} \exp(-E_a^d/kT) \text{ cm}^{-2} \text{ sec}^{-1}, \quad (5)$$

where θ_{ij} is the fractional coverage of the desorbing species (e.g., if the molecule AB is dissociatively adsorbed on the surface, then the proper θ_{ij} to use is $\theta_A\theta_B$; whereas if AB is associately adsorbed, then $\theta_{ij} = \theta_{AB}$); E_a^d is the activation energy to desorption; and the preexponential factor of 10^{28} is a product of a surface adsorption site concentration and a partition function ratio. The reaction of two adsorbed species (i.e., heterogeneous catalysis following Langmuir-Hinshelwood kinetics) may be analyzed using absolute rate theory, and the result is very similar to that obtained for desorption [Eq. (5) above] viz (*13, 14*)

$$R_r^{\text{L-H}} \simeq 10^{28}\theta_i\theta_j \exp(-E_a^{\text{L-H}}/kT) \text{ cm}^{-2} \text{ sec}^{-1} \quad (6)$$

where $E_a^{\text{L-H}}$ is the activation energy to the surface reaction between adspecie i and adspecie j whose respective fractional surface coverages are θ_i and θ_j.

Equations (3)–(6) may be used to estimate the rates of the following gas–surface interactions: adsorption, catalysis with Rideal-Eley kinetics, desorption, and catalysis with Langmuir-Hinshelwood kinetics, respectively. The BEBO model may be used to estimate the relevant activation energies, so *a priori* calculations of the rates of the various elementary surface reactions may be made. The absolute rate theory–bond energy bond order (ART-BEBO) model will be illustrated in detail for the various elementary processes which may occur when an N_2O molecule interacts with both a clean and a C covered Pt surface. For completeness the adsorption of both N_2 and O_2 is also considered. This is a very convenient gas–surface system to consider since it is sufficiently complicated to illustrate all of the concepts of the ART-BEBO model, and some comparisons can be made between the model calculations and recent molecular beam data of West and Somorjai (*12*). The BEBO correlations (*4*) which are required in performing the model calculations are shown in Fig. 1. Since the spectroscopic BEBO correlations are only applicable for bond orders greater than unity (see Fig. 1), a linear extrapolation must be made for bond orders less than unity, i.e., the bond energy in this case is given by the single order bond energy multiplied by bond order. This is known to be a very good approximation for σ-type bonding (*4, 5*).

Calculated Results

The BEBO model will now be used to calculate the activation energies of the most probable surface events when an N_2O molecule interacts with a clean or a C covered Pt surface. Initially the adsorption of N_2 will be considered,

$$2\text{Pt} + \text{N}_2(\text{g}) \rightarrow 2\text{Pt}{=}\text{N}, \quad (7)$$

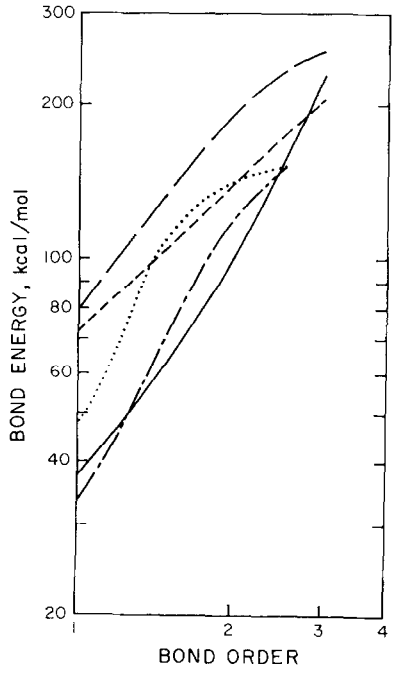

FIG. 1. Bond energy bond order relations for the following bonds: (— —) CO; (- - -) CN; (· · · ·) NO; (— -) OO; (—) NN.

The interaction energy for this reaction according to Eq. (1) may be written as

$$V = D_{N_2} - E_{N_2,S} - E_{PtN_2}. \quad (8)$$

In Eq. (8) D_{N_2} is known to be 226 kcal/mol (*4*), $E_{N_2,S}$ may be found as a function of bond order from Fig. 1, and E_{PtN_2} is given by Eq. (2) with $E_{PtN_2,S} = 40$ kcal/mol (*8*), i.e.,

$$E_{PtN_2} = 40n_{PtN_2}. \quad (9)$$

The bond conservation equations which relate the bond order in the N_2 molecule to that in the Pt–N_2 "surface molecule" are given by

$$\begin{aligned} n_{N_2} &= 3 - 0.5n_{PtN_2}, \\ n_{PtN_2} &= n_{PtN_2}, \\ n_{Pt-Pt} &= 3 - 0.5n_{PtN_2}, \end{aligned} \quad (10)$$

where $0 \leq n_{PtN_2} \leq 6$ since the product of the adsorption reaction is two triply bonded N atoms to the Pt surface. The quantity n_{Pt-Pt} is the free surface valence of the Pt, and a part of this surface valency is reduced by the formation of coordination bonding as the adsorption reaction proceeds. The interaction energy between N_2 and the Pt surface calculated using Eqs. (8)–(10) is shown in Fig. 2. There is an activation energy to adsorption of ~46 kcal/mol and the heat of adsorption is ~ −14 kcal/mol. Thus, the activation energy for *desorption* of the adatoms as an N_2 molecule is ~60 kcal/mol.

The adsorption of O_2 on Pt may be written as

$$2\,Pt + O_2(g) \rightarrow 2\,Pt{=}O, \quad (11)$$

and the energy of interaction is given by

$$V = D_{O_2} - E_{O_2,S} - E_{PtO_2}. \quad (12)$$

The dissociation energy of an O_2 molecule, D_{O_2}, is 118 kcal/mol (*4*), a value for $E_{O_2,S}$ may be found from Fig. 1 as a function of n_{O_2}, and a value for E_{PtO_2} may be calculated using the following equation

$$E_{PtO_2} = 46.6n_{PtO_2}, \quad (13)$$

since the bond energy of a single order Pt–O_2 bond is 46.6 kcal/mol (*6, 7, 11*). The bond conservation relations may be written as follows:

$$\begin{aligned} n_{O_2} &= 2 - 0.5n_{PtO_2}, \\ n_{PtO_2} &= n_{PtO_2}, \\ n_{Pt-Pt} &= 2 - 0.5n_{PtO_2}, \end{aligned} \quad (14)$$

where $0 \leq n_{PtO_2} \leq 4$, as may be seen from Eq. (11). The interaction energy of O_2 with Pt calculated according to Eqs. (12)–(14) is shown in Fig. 2. There is an activation energy to adsorption of ~2 kcal/mol and the heat of adsorption is ~69 kcal/mol. Thus, the activation energy to desorption is ~71 kcal/mol. The BEBO model predicts no stable molecularly adsorbed state for either N_2 or O_2 on Pt.

It is possible for N_2O to adsorb on Pt in two distinctly different ways—either through an N atom with NO being liberated into the gas phase, or through the O atom with N_2 liberated into the gas phase. These two adsorption mechanisms will each be analyzed in turn. For the first mechanism

$$Pt + N{\equiv}N{\cdots}O(g) \rightarrow Pt{\equiv}N + N{\equiv}O(g), \quad (15)$$

the interaction energy is given by

$$V = D_{N_2O} - E_{N_2O,S} - E_{PtN}, \quad (16)$$

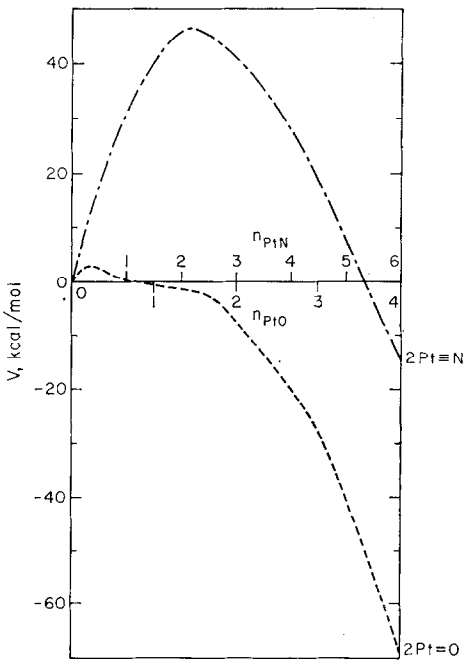

FIG. 2. Calculated energetics for the following reactions: (——) $2Pt + N_2(g) \rightarrow 2Pt{\equiv}N$; (– – –) $2Pt + O_2(g) \rightarrow 2Pt{=}O$.

and D_{N_2O} is known to be 267 kcal/mol (4), $E_{N_2O,S}$ may be found from Fig. 1, and E_{PtN} is given by Eq. (9). In the gaseous N_2O molecule the NN and NO bond orders are 2.5 and 1.5, respectively, and the bond order of the gaseous NO molecule is 2.5 (4). The appropriate bond conservation equations are the following:

$$\begin{aligned} n_{NN} &= 2.5 - 0.833n_{PtN}, \\ n_{NO} &= 1.5 + 0.333n_{PtN}, \\ n_{PtN} &= n_{PtN}, \\ n_{Pt-Pt} &= 1.5 - 0.5n_{PtN}, \end{aligned} \quad (17)$$

where $0 \leq n_{PtN} \leq 3$. The interaction energy calculated using Eqs. (16) and (17) is shown as a function of n_{PtN} in Fig. 3. There is an activation energy to this adsorption reaction of ~15.5 kcal/mol, and the reaction is exothermic by ~5 kcal/mol.

The alternate mechanism for the adsorption of N_2O may be written as

$$Pt + O\cdots N{=}{=}N(g) \rightarrow Pt = O + N{\equiv}N(g). \quad (18)$$

The energy of interaction of N_2O with Pt according to the mechanism of Eq. (18) is the following:

$$V = D_{N_2O} - E_{N_2O,S} - E_{PtO}. \quad (19)$$

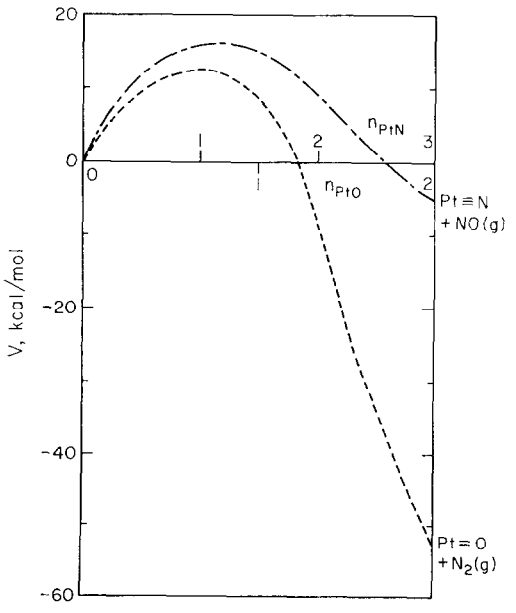

FIG. 3. Calculated energetics for the following reactions: (——) $Pt + N_2O(g) \rightarrow Pt{\equiv}N + NO(g)$; (– – –) $Pt + N_2O(g) \rightarrow Pt{=}O + N_2(g)$.

with $D_{N_2O} = 267$ kcal/mol and $E_{N_2O,S}$ given by Fig. 1 just as for the mechanism of Eq. (15), and E_{PtO} may be calculated using Eq. (13). The bond conservation equations which apply to the adsorption mechanism of Eq. (18) are the following:

$$\begin{aligned} n_{NN} &= 2.5 + 0.25n_{PtO}, \\ n_{NO} &= 1.5 - 0.75n_{PtO}, \\ n_{PtO} &= n_{PtO}, \\ n_{Pt-Pt} &= 1 - 0.5n_{PtO}, \end{aligned} \quad (20)$$

where $0 \leq n_{PtO} \leq 2$. The interaction energy calculated from Eqs. (19) and (20) is shown as a function of n_{PtO} in Fig. 3. There is an activation energy to adsorption of ~12.5 kcal/mol, and the adsorption reaction is exothermic by ~52 kcal/mol.

Adsorption reactions analogous to Eqs. (15) and (18) may also be written for the adsorption of N_2O on a C covered Pt surface, henceforth denoted by PtC. The reaction analogous to Eq. (15) may be written as

$$Pt{\equiv}C + N{=}{=}N\cdots O(g) \rightarrow Pt{=}C{=}N + N{=}{=}O(g). \quad (21)$$

It is convenient to analyze the reaction of Eq. (21) in two steps, the first of which applies for $0 \leq n_{CN} \leq 1$ and the second of which applies for $1 \leq n_{CN} \leq 2$. This is due to the fact that the adsorbed C atom has one free valence electron present (7) which is available in the formation of a first order CN bond prior to perturbing the Pt≡C bonds. The interaction energy for the first step mentioned above is the following:

$$V = D_{N_2O} - E_{N_2O,S} - E_{CN}, \quad (22)$$

where $D_{N_2O} = 267$ kcal/mol, and both $E_{N_2O,S}$ and E_{CN} may be found as a function of bond order from Fig. 1. The bond conservation equations applicable to the reaction of Eq. (21) are the following:

$$\begin{aligned} n_{NN} &= 2.5 - 1.5n_{CN}, \\ n_{NO} &= 1.5 + n_{CN}, \\ n_{CN} &= n_{CN}, \\ n_{C\cdot} &= 0.5(1 - n_{CN}), \end{aligned} \quad (23)$$

where $0 \leq n_{CN} \leq 1$, and $n_{C\cdot}$ represents the free radical nature of the adsorbed C atom (7). For $1 \leq n_{CN} \leq 2$ there is a breaking of

the Pt≡C bonds and the relationship describing the interaction energy is modified somewhat, viz,

$$V = D_{N_2O} + D_{PtC} - E_{N_2O,S} - E_{CN} - E_{PtC}, \quad (24)$$

where $D_{PtC} = 189$ kcal/mol [a third order bond with single order bond energy of 63 kcal/mol (*6*, *7*, *10*)], $E_{N_2O,S}$ and E_{CN} may be obtained from Fig. 1 as a function of bond order just as before, and E_{PtC} is given by (*6*, *7*, *10*)

$$E_{PtC} = 63n_{PtC}. \quad (25)$$

The bond conservation applicable to Eq. (24) are the following:

$$\begin{aligned} n_{NN} &= 1 - n'_{CN}, \\ n_{NO} &= 2.5, \\ n_{CN} &= 1 + n'_{CN}, \\ n_{PtC} &= 3 - n'_{CN}, \\ n_{Pt-Pt} &= n'_{CN}, \end{aligned} \quad (26)$$

where $0 \leq n'_{CN} \leq 1$ (or equivalently, $1 \leq n_{CN} \leq 2$). The interaction energy between an N_2O molecule and a PtC surface according to the mechanism of Eq. (21) may be calculated using Eqs. (22)–(26) and the result is shown in Fig. 4. There is an activation energy to the reaction of ~36 kcal/mol, and the reaction is endothermic by that same amount of energy. As may be seen from Fig. 4, there is a quasi-stable endothermic potential minimum which occurs at $n_{PtC} = 3$, $n_{CN} = n_{NN} = 1$ and $n_{NO} = 2.5$. It should be noted that if the final adsorbed state is Pt—C≡N rather than Pt=C=N, the energetics of the reaction are essentially unchanged. The reaction is endothermic with an activation energy of ~34 kcal/mol rather than 36 kcal/mol.

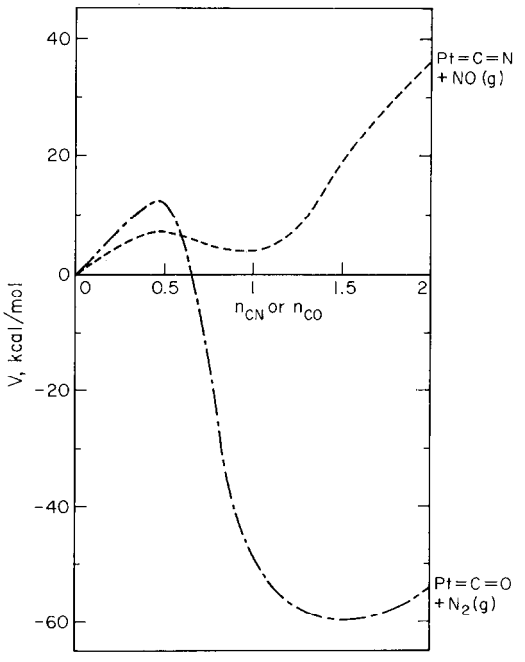

FIG. 4. Calculated energetics for the following reactions: (— –) Pt≡C + N_2O(g) → Pt=C=O + N_2(g); (– – –) Pt≡C + N_2O(g) → Pt=C=N + NO(g).

The alternate way in which N_2O may adsorb on PtC is the analogue of Eq. (18) for clean Pt, namely

$$Pt{\equiv}C + O\cdots N{\equiv}N(g) \rightarrow Pt{=}C{=}O + N{\equiv}N(g). \quad (27)$$

As before it is convenient to examine this reaction in two steps, the first step occurring when $0 \leq n_{CO} \leq 1$, and the second step when $1 \leq n_{CO} \leq 2$. The first step occurs without the breaking of Pt≡C bonds, and the interaction energy for this case is given by

$$V = D_{N_2O} - E_{N_2O,S} - E_{CO}, \quad (28)$$

where $D_{N_2O} = 267$ kcal/mol, and $E_{N_2O,S}$ and E_{CO} are obtained from Fig. 1 as a function of bond order. The bond conservation equations which apply to this reaction are the following:

$$\begin{aligned} n_{NN} &= 2.5 + 0.5n_{CO}, \\ n_{NO} &= 1.5 - n_{CO}, \\ n_{CO} &= n_{CO}, \\ n_{C} &= 0.5(1 - n_{CO}), \end{aligned} \quad (29)$$

where $0 \leq n_{CO} \leq 1$. When the bond order of the CO bond increases above unity, there is a breaking of the Pt≡C bonding. Then the interaction energy may be written as

$$V = D_{N_2O} + D_{PtC} - E_{N_2O,S} - E_{CO} - E_{PtC}, \quad (30)$$

where $D_{PtC} = 189$ kcal/mol, E_{PtC} is given by Eq. (25) and the other terms of Eq. (30) are as defined previously. The bond conservation relations which apply in this case are the following:

$$\begin{aligned} n_{NN} &= 3, \\ n_{NO} &= 0.5(1 - n'_{CO}), \\ n_{PtC} &= 3 - n'_{CO}, \\ n_{CO} &= 1 + n'_{CO}, \\ n_{Pt-Pt} &= 0.5n'_{CO}, \end{aligned} \tag{31}$$

where $0 \leq n'_{CO} \leq 1$ (i.e., $1 \leq n_{CO} \leq 2$). When $1 \leq n_{CO} \leq 2$, the value of E_{PtC} in Eq. (30) is no longer given by Eq. (25) since the bond energy of the single order Pt–CO bond is not equal to that of a single order Pt–C bond. The former is 46 kcal/mol, whereas the latter is 63 kcal/mol (*6*, *7*). Thus, for $1 \leq n_{CO} \leq 2$ the value of E_{PtC} is given by (*6*, *7*)

$$E_{PtC} = [63 - 17(3 - n_{PtC})]n_{PtC}. \tag{32}$$

The energetics of the interaction of N_2O with PtC according to the mechanism of Eq. (27) and calculated using Eqs. (28)–(32), is shown in Fig. 4. There is an activation energy to adsorption of ~12 kcal/mol, a weak minimum of depth ~ −59 kcal/mol at $n_{CO} = 1.5$, and a heat of reaction of ~ −54 kcal/mol.

The calculated results for the various adsorption reactions of O_2, N_2, and N_2O on clean Pt and of N_2O on PtC have been presented in Figs. 2, 3, and 4. Attention will now be given to the various reactions which regenerate the clean Pt surface. Two such reactions, namely the desorption of N_2 and O_2 are analyzed in Fig. 2, i.e., the activation energy for desorption of N_2 and O_2 is 60 and 71 kcal/mol, respectively. Another reaction which will free the Pt surface of adsorbed O atoms is the Rideal-Eley type interaction with an impinging N_2O molecule. There are two cases to consider—one of which results in the formation of two NO molecules, and the other of which results in the formation of an N_2 molecule and an O_2 molecule. These two cases will now be treated each in turn.

The reaction of an N_2O molecule with an adsorbed O atom on a Pt surface following Rideal-Eley kinetics leading to the formation of two NO molecules may be written as

$$\text{Pt}{=}\text{O} + \text{N}{\equiv}\text{N}'{\cdots}\text{O}'(g) \rightarrow \text{Pt} + \text{N}{\equiv}\text{O}(g) + \text{N}'{\equiv}\text{O}'(g). \tag{33}$$

The interaction energy describing this surface reaction is given by

$$V = D_{N_2O} + D_{PtO} - E_{N_2O,S} - E_{NO} - E_{PtO}, \tag{34}$$

with $D_{N_2O} = 267$ kcal/mol, $D_{PtO} = 93.2$ kcal/mol, $E_{N_2O,S}$ and E_{NO} given in Fig. 1 as a function of bond order, and with E_{PtO} given by Eq. (13). The bond conservation relations which apply to Eq. (33) are the following.

$$\begin{aligned} n_{NN'} &= 2.5 - n_{NO}, \\ n_{N'O'} &= 1.5 + 0.4n_{NO}, \\ n_{PtO} &= 2 - 0.8n_{NO}, \\ n_{NO} &= n_{NO}, \\ n_{Pt-Pt} &= 0.4n_{NO}, \end{aligned} \tag{35}$$

where $0 \leq n_{NO} \leq 2.5$. The energetics of the reaction of Eq. (33) calculated according to Eqs. (34) and (35) is shown in Fig. 5. The reaction is endothermic by ~53 kcal/mol, and the activation energy to reaction is also ~53 kcal/mol. There is a quasi-stable endothermic energy minimum at $n_{NO} \cong 1.5$ as may be seen in Fig. 5.

The alternate mechanism whereby an

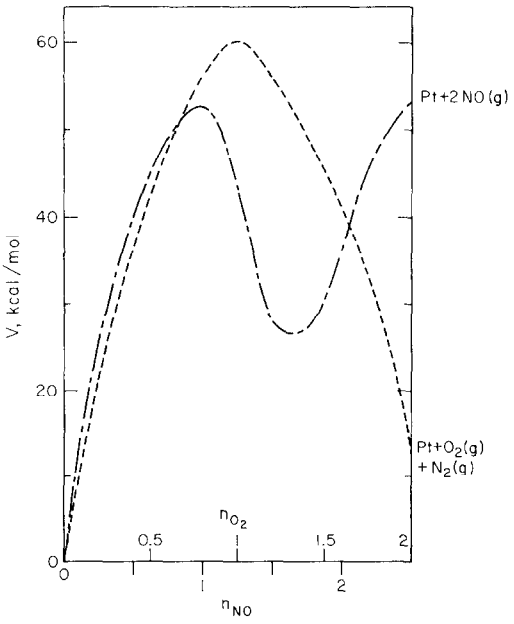

FIG. 5. Calculated energetics for the following reactions: (— –) $\text{Pt}{=}\text{O} + N_2O(g) \rightarrow \text{Pt} + 2\text{NO}(g)$; (– – –) $\text{Pt}{=}\text{O} + N_2O(g) \rightarrow \text{Pt} + N_2(g) + O_2(g)$.

N_2O molecule may react with an adsorbed O atom with Rideal-Eley kinetics is the following:

$$Pt{=}O + O'{\cdots}N{\equiv}N'(g) \rightarrow Pt + O{=}O'(g) + N{\equiv}N'(g). \quad (36)$$

The energetics of this interaction are very similar to Eq. (34), namely

$$V = D_{N_2O} + D_{PtO} - E_{N_2O,S} - E_{OO'} - E_{PtO}, \quad (37)$$

and all the quantities of Eq. (37) may be evaluated according to the methods given below Eq. (34). The bond conservation relations which apply to this reaction mechanism are the following:

$$\begin{aligned} n_{O'N} &= 1.5 - 0.75n_{OO'}, \\ n_{NN'} &= 2.5 + 0.25n_{OO'}, \\ n_{PtO} &= 2 - n_{OO'}, \\ n_{OO'} &= n_{OO'}, \\ n_{Pt-Pt} &= 0.5n_{OO'}, \end{aligned} \quad (38)$$

with $0 \leq n_{OO'} \leq 2$. The energy of interaction for the reaction of Eq. (36) calculated using Eqs. (37) and (38) is shown in Fig. 5 as a function of $n_{OO'}$. The reaction is endothermic by ~13 kcal/mol, and there is an activation energy to reaction of ~60 kcal/mol.

Attention will now be focused on the ways in which adsorbed N atoms may be removed from the Pt surface by impinging N_2O molecules considering Rideal-Eley kinetics. Just as for the removal of adsorbed O atoms from the surface considered above, there are two possible reaction mechanisms. The Pt≡N complex can either interact with an N atom or the O atom in the N_2O molecule. The variant between this reaction and the one with Pt=O is that the product of this reaction is the same independent of the detailed mechanism, namely an N_2 and an NO molecule. However, the kinetics of the two possible reaction mechanisms are substantially different as shown below.

The first case to be considered is the interaction of the O atom in the N_2O molecule with the adsorbed N atom. This reaction may be written as

$$Pt{\equiv}N + O{\cdots}N'{=}N(g) \rightarrow Pt + N{=}O(g) + N'{\equiv}N(g). \quad (39)$$

The energetics of the reaction given by Eq. (39) are given by

$$V = D_{N_2O} + D_{PtN} - E_{N_2O,S} - E_{NO} - E_{PtN}, \quad (40)$$

where $D_{N_2O} = 267$ kcal/mol, $D_{PtN} = 120$ kcal/mol, $E_{N_2O,S}$ and E_{NO} given in Fig. 1, and E_{PtN} is given by Eq. (9). The bond conservation relations which apply to Eq. (39) are the following:

$$\begin{aligned} n_{N'N} &= 2.5 + 0.2n_{NO}, \\ n_{ON'} &= 1.5 - 0.6n_{NO}, \\ n_{PtN} &= 3 - 1.2n_{NO}, \\ n_{NO} &= n_{NO}, \\ n_{Pt-Pt} &= 0.6n_{NO}, \end{aligned} \quad (41)$$

where $0 \leq n_{NO} \leq 2.5$. The results of the calculated interaction energy are shown in Fig. 6 as a function of n_{NO}. The reaction is endothermic by ~6 kcal/mol and the activation energy to reaction is ~45 kcal/mol. A weak endothermic potential minimum of $V \sim 3$ kcal/mol is predicted at the point when $n_{NO} = 2$.

The alternate Rideal-Eley type reaction in which N_2O reacts with an adsorbed N atom to form an N_2 and an NO molecule is the following

$$Pt{\equiv}N + N{=}N'{\cdots}O(g) \rightarrow Pt + N{\equiv}N(g) + N'{=}O(g). \quad (42)$$

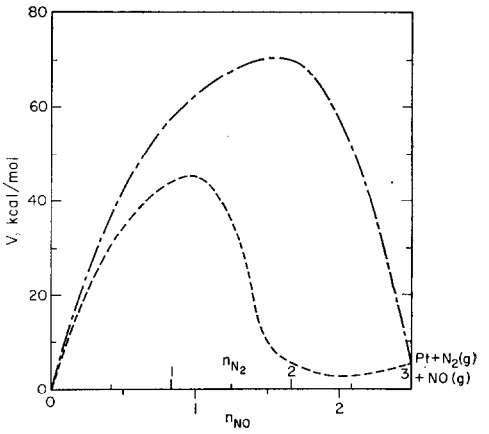

FIG. 6. Calculated energetics for the following reactions: (——) Pt≡N + NN'O(g) → Pt + NN(g) + N'O(g); (- - -) Pt≡N + ON'N(g) → Pt + NO(g) + N'N(g).

The energetics of the reaction described in Eq. (42) may be written as

$$V = D_{N_2O} + D_{PtN} - E_{N_2O,S} - E_{NN} - E_{PtN}, \quad (43)$$

and the strong similarity with Eq. (40) should be noted. The bond conservation relations which apply to the reaction of Eq. (42) are the following:

$$\begin{aligned} n_{NN'} &= 2.5 - 0.833n_{NN}, \\ n_{N'O} &= 1.5 + 0.333n_{NN}, \\ n_{PtN} &= 3 - n_{NN}, \\ n_{NN} &= n_{NN}, \\ n_{Pt-Pt} &= 0.5n_{NN}, \end{aligned} \quad (44)$$

with $0 \leq n_{NN} \leq 3$. The energy of interaction calculated according to Eqs. (43) and (44) is shown in Fig. 6. As pointed out previously, the initial and final states of the reactions of Eqs. (39) and (42) are identical. However, the kinetics of Eq. (42) are substantially less favorable with an activation energy of ~70 kcal/mol.

A final way in which a clean Pt surface may be regenerated from one on which O and N atoms are adsorbed is the surface reaction (Langmuir-Hinshelwood kinetics) of the adsorbed atoms to form an NO molecule. That reaction may be written as

$$Pt{\equiv}N + Pt{=}O \rightarrow 2Pt + N{\equiv}O(g). \quad (45)$$

The energetics of this reaction are described by the following equation:

$$V = D_{PtN} + D_{PtO} - E_{PtN} - E_{PtO} - E_{NO}, \quad (46)$$

where $D_{PtN} = 120$ kcal/mol, $D_{PtO} = 93.2$ kcal/mol, E_{PtN} and E_{PtO} are given by Eqs. (9) and (13), respectively, and E_{NO} may be found as a function of bond order from Fig. 1. The bond conservation relationships applicable to the reaction of Eq. (45) are the following:

$$\begin{aligned} n_{PtN} &= 3 - 1.2n_{NO}, \\ n_{PtO} &= 2 - 0.8n_{NO}, \\ n_{NO} &= n_{NO}, \\ n_{Pt-Pt} &= n_{NO}, \end{aligned} \quad (47)$$

with $0 \leq n_{NO} \leq 2.5$. The interaction energy for this Langmuir-Hinshelwood type catalytic reaction is shown in Fig. 7 as a function of n_{NO}. The reaction is endothermic by ~61 kcal/mol, and the activation energy to reaction is equal to its endothermicity. As may be seen from Fig. 7 there is a quasi-stable endothermic minimum in the potential energy diagram at a value of $n_{NO} \cong 1.5$. This corresponds to a molecularly adsorbed state of the NO molecule on the Pt surface.

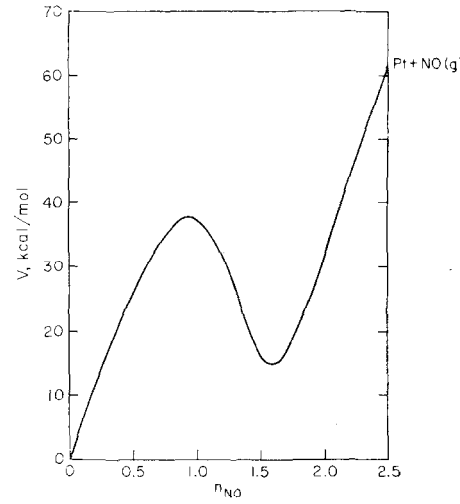

FIG. 7. Calculated energetics for the reaction: Pt=O + Pt≡N → 2Pt + NO(g).

DISCUSSION

The major contribution of this work is to show the way in which the empirical BEBO model may be used to make a priori estimates of activation energies of elementary surface reactions, e.g., adsorption, desorption, or heterogeneously catalyzed reactions obeying either Rideal-Eley or Langmuir-Hinshelwood kinetics. Detailed calculations have been made for most of the relevant reactions which occur when N_2O interacts with either a clean or a C covered Pt surface. These reactions together with the respective activation energies and heats of reaction are summarized in Table 1. It is useful to apply the BEBO model to this gas–surface system since reactive scattering measurements of an N_2O molecular beam from these surfaces have recently been reported (*12*). When the activation energies calculated using the BEBO model are used in conjunction with the absolute rate theory,

TABLE 1

CALCULATED REACTION RATES, ACTIVATION ENERGIES AND HEATS OF REACTION FOR THE ELEMENTARY SURFACE REACTIONS WHICH OCCUR WHEN N_2O INTERACTS WITH CLEAN AND C COVERED Pt[a]

Reaction	E_a (kcal/mol)[b]	ΔH (kcal/mol)	Rate (cm^{-2} sec^{-1})
1. Pt≡N + Pt≡N → 2Pt + N_2(g)	60	+14	7.0×10^{7}
2. Pt=O + Pt=O → 2Pt + O_2(g)	71	+69	2.7×10^{10}
3. Pt + N_2O(g) → Pt≡N + NO(g)	15.5	−5	1.0×10^{10}
4. Pt + N_2O(g) → Pt=O + N_2(g)	12.5	−52	3.8×10^{10}
5. Pt=O + N_2O(g) → Pt + N_2(g) + O_2(g)	60	+13	0.3
6. Pt=O + N_2O(g) → Pt + 2NO(g)	53	+53	6.7
7. Pt≡N + N_2O(g) → Pt + N_2(g) + NO(g)	45	+6	1.1
8. Pt≡N + Pt=O → 2Pt + NO(g)	61	+61	9.8×10^{9}
9. Pt≡C + N_2O(g) → Pt=C=N + NO(g)	36	+36	1.1×10^{6}
10. Pt≡C + N_2O(g) → Pt=C=O + N_2(g)	12	−54	4.8×10^{10}

[a] Conditions: T = 1125°K and $p_{N_2O} \sim 10^{-8}$ Torr, i.e., an impingement flux of 10^{13} cm^{-2} sec^{-1}.
[b] E_a is the activation energy to the elementary surface reaction given in the first column.

it is possible to predict absolute magnitudes for the *rates* of the various surface reactions. Using reasonable values for the pre-exponential of the rate coefficients, it was shown above that the appropriate rate expressions for adsorption, surface reactions obeying Rideal-Eley kinetics, desorption, and surface reactions obeying Langmuir-Hinshelwood kinetics are given by Eqs. (3), (4), (5) and (6), respectively.

The rates of the 10 reactions discussed in the previous section may be calculated employing the experimental conditions of West and Somorjai (*12*), namely T = 1125°K and an impingement flux of N_2O molecules of $\sim 10^{13}$ cm^{-2} sec^{-1}. In order to calculate the rates of reactions 1, 2, 5, 6, 7, and 8 of Table 1, the equilibrium coverages of both N and O atoms must be known. These coverages may be easily calculated by using the absolute rate equations and equating the total rate of adsorption and that of desorption for both N and O atoms. Solving the two resulting coupled quadratic equations simultaneously gives

$$\theta_N \cong 5.1 \times 10^{-5}, \qquad \theta_O \cong 1.2 \times 10^{-2}, \tag{48}$$

for the coverages of N and O atoms, respectively, for T = 1125°K and $p/(2\pi mkT)^{1/2}$ = 10^{13} molecules/cm^2 sec. Using these coverages the rates of the surface reactions are readily calculated, and the results are shown in Table 1. It should be noted that the rates of the surface reactions obeying Rideal-Eley kinetics proceed at a negligible rate (reactions 5, 6, and 7 of Table 1). The O atoms are removed from the clean Pt at an appreciable rate by both reactions 2 and 8, whereas only reaction 8 contributes significantly to the removal of N atoms from the Pt.

Neither the clean Pt surface nor the PtC surface is exceedingly efficient at dissociating N_2O. Both surfaces dissociate ~0.5% of the impinging N_2O molecules (for clean Pt the sum of the rates of reactions 3 and 4 or for PtC the rate of reaction 10, both divided by the impingement flux, namely 10^{13} molecules/cm^2 sec).

It is interesting to compare the expected scattering distributions of NO produced when N_2O adsorbs on either Pt or PtC, i.e., reactions 3 and 9 in Table 1. On PtC the reaction is a direct scattering process with the NO evolved as the surface CN bond forms. The energetics of the following reaction under the conditions of temperature and pressure of Ref. (*12*) are so unfavorable as to not necessitate its consideration:

$$\text{Pt=C=N} + \text{Pt=C=O} \rightarrow 2\text{Pt}\equiv\text{C} + \text{N}\equiv\text{O(g)}. \tag{49}$$

Thus, it would be expected that the NO reflected from a PtC surface as a result of the dissociation of N_2O would not be

emitted with a random (cosine) distribution, but rather should be emitted with a distribution peaked near the specularly reflected angle, i.e., the NO molecule does not necessarily accommodate to the surface temperature. On the other hand, approximately half of the NO emitted from the clean Pt surface is desorbed according to reaction 8 of Table 1. Thus, the spatial distribution of NO emitted from clean Pt would be expected to be much more nearly cosine indicating energy accommodation to the surface temperature.

It is possible to compare the calculated results with the experimental results of West and Somorjai (*12*) in a least a qualitative way. Unfortunately, due to the presence of a large background pressure of CO it was impossible to monitor experimentally either reflected N_2 or CO. However, the reflected NO was monitored mass spectrometrically. Although more definitive experiments are required to fully test the model predictions, the following observations agree with the ART-BEBO model: (1) The Pt surfaces dissociate N_2O very poorly, on the order of a percent of the impinging N_2O molecules; and (2) The spatial distribution of the NO molecules is peaked toward the specularly reflected angle for the PtC surface indicating a direct reaction without full accommodation at the surface, while the NO emitted by the clean Pt surface is much more diffuse indicating a greater energy accommodation at the surface. The expected importance of the desorption of CO from the PtC surface was also confirmed experimentally: It was necessary to replenish the C overlayer on the Pt by exposure to C_2H_2 after extensive scattering of N_2O from the PtC surface.

The experimental observation of a "ring structure" in the low-energy electron diffraction pattern for the C overlayer on the Pt surface indicates much of the surface is covered by the basal plane of graphite (*12*). However, the N_2O almost certainly reacts preferentially with carbide type C rather than the basal plane of graphite. There is no free valence electron in the graphite to interact with an adsorbing N_2O molecule. Also, to remove a C atom from a graphite overlayer requires breaking three effectively 1.53 order CC bonds, i.e., $\sim 3 \times 117 = 351$ kcal/mol. Removing a C atom from the carbide requires only $3 \times 63 = 189$ kcal/mol (*10*). The graphite is much more stable and hence less reactive. Consider the reaction

$$C(s) + N{=}N{=}O(g) \xrightarrow{Pt} N{\equiv}N(g) + C{\equiv}O(g). \quad (50)$$

This reaction is exothermic by 26 kcal/mol for carbide type C, i.e., $[(3 \times 63 + 267) - (226 + 256)] = -26$ kcal/mol, although there is a calculated activation energy of ~ 12 kcal/mol as shown in Fig. 4. However, for graphitic type C, the reaction is *endothermic by 136 kcal/mol,* i.e., $[3 \times 117 + 267) - (226 + 256)] = +136$ kcal/mol. Thus, it is very reasonable to expect that the reactions of N_2O with a C covered Pt surface proceed almost exclusively on carbide sites rather than on the smooth basal plane of graphite. The relative passivity of the basal plane of graphite to reaction with a beam of molecular oxygen has recently been demonstrated by Olander and coworkers (*15*).

In conclusion, the ART-BEBO model has been described and applied to analyze in detail the interaction of N_2O with Pt and PtC surfaces. As has been discussed in detail elsewhere, the BEBO model is expected to give activation energies accurate to within a few kilocalories per mole (*5*, *11*). The absolute rate theory aspects of the model calculation would be expected to yield preexponential factors of the various rate coefficients accurate to within perhaps an order of magnitude. The close agreement between the calculated and observed fraction of N_2O molecules dissociated by Pt tends to indicate the accuracy of the ART-BEBO model. The good agreement between the calculated results and the experimental data offers the hope that the ART-BEBO model may prove exceedingly useful in predicting the kinetics of both numerous as well as diverse types of elementary surface reactions.

Acknowledgment

It is a pleasure to acknowledge the financial assistance of the Division of Chemistry and Chem-

ical Engineering of the California Institute of Technology.

REFERENCES

1. BOND, G. C., *Discuss. Faraday Soc.* **41**, 200 (1966).
2. BREWER, L., *in* "Phase Stability in Metals and Alloys" (P. Rudman, J. Stringer and R. I. Jaffee, Eds.), McGraw-Hill, New York, 1967.
3. BREWER, L., *Science* **161**, 115 (1968).
4. JOHNSTON, H. S., *"Gas Phase Reaction Rate Theory."* Ronald Press, New York, 1966.
5. WEINBERG, W. H., AND MERRILL, R. P., I. *Surface Sci.* **33**, 493 (1972).
6. WEINBERG, W. H., AND MERRILL, R. P., II. *Surface Sci.*, in press.
7. WEINBERG, W. H., LAMBERT, R. M., COMRIE, C. M., AND LINNETT, J. W., *Surface Sci.* **30**, 299 (1972).
8. WEINBERG, W. H., AND MERRILL, R. P., III. *Surface Sci.*, in press.
9. WEINBERG, W. H., AND MERRILL, R. P., I. *J. Catal.*, in press.
10. WEINBERG, W. H., AND MERRILL, R. P., II. *J. Catal.*, in press.
11. WEINBERG, W. H., presented: *19th Nat. Vac. Symp. Amer. Vac. Soc. Chicago, IL, Oct. 1972; J. Vac. Sci. Technol.* **10**(1), (1973).
12. WEST, L. A., AND SOMORJAI, G. A., *J. Vac. Sci. Technol.* **9**, 668 (1972).
13. LAIDLER, K. J., "Chemical Kinetics," 2nd ed., McGraw-Hill, New York, 1965.
14. WEINBERG, W. H., unpublished data.
15. OLANDER, D. R., SIEKHAUS, W., JONES, R., AND SCHWARZ, J. A., *J. Chem. Phys.* **57**, 408 (1972).