

KINETICS OF NITROGEN ADSORPTION ON Fe(111)

G. ERTL, S.B. LEE and M. WEISS

Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, D-8000 München 2, Germany

Received 27 May 1981; accepted for publication 7 October 1981

The dissociative adsorption of nitrogen on a clean Fe(111) surface proceeds via $N_2 \xrightleftharpoons[-1]{1} N_{2,ad} \xrightarrow{2} 2N_s$ with a very small overall sticking coefficient and a slightly negative activation energy: $\sigma_0 = 2.2 \times 10^{-6} \exp(-E^*/RT)$; $E^* = -0.8$ kcal/mole (at zero coverage). The intermediate formed $N_{2,ad}$ is characterized by an adsorption energy of 7.5 kcal/mole and by a dipole moment of ~ 0.4 D of the adsorbate complex, the negative charge being located at the nitrogen molecule. The kinetic parameters of the individual (first order) steps were determined as follows: (i) $s_0 \approx 10^{-2 \pm 0.5}$ (sticking coefficient into the molecular state $\hat{=} k_1$); (ii) $k_{-1} = \nu_{-1} \exp(-E_1/RT)$ with $\nu_{-1} = 10^{10 \pm 1} \text{ s}^{-1}$, $E_1 = 7.5$ kcal/mole (desorption of $N_{2,ad}$); (iii) $k_2 = \nu_2 \exp(-E_2/RT)$, with $\nu_2 \approx 10^7 \text{ s}^{-1}$, $E_2 = E_1 + E^* = 6.7$ kcal/mole (dissociation of $N_{2,ad}$ into $2N_s$). The extremely low dissociation probability of gaseous N_2 is caused by two factors, namely unusually low values for s_0 and for the ratio ν_2/ν_{-1} .

1. Introduction

Dissociative adsorption of nitrogen on iron surfaces comprises the rate-limiting step in the catalytic synthesis of ammonia [1]. A detailed investigation of the microscopic steps involved is therefore a necessary prerequisite for the understanding of this important process. Previous studies from our laboratory [2,3] were concerned with the properties of the atomic nitrogen species, N_s , held at iron single crystal surfaces. It turned out that the apparent activation energy for the overall process $N_2 \rightarrow 2N_s$ is rather low, but that its effective rate ($=$ sticking coefficient) is nevertheless very small ($\lesssim 10^{-6}$). During these studies it became evident that a weakly held molecular species, $N_{2,ad}$, is intermediately formed which acts as "precursor" for dissociative adsorption. Direct photoelectron spectroscopic evidence for the existence of molecularly and atomically adsorbed nitrogen on polycrystalline Fe surfaces was obtained by Roberts and his coworkers [4,5]. Information on the heat of adsorption of molecular nitrogen on iron films is available from the work of Wedler et al. [6] as well as from earlier studies by Beeck et al. [7]. The present work is mainly concerned with the kinetics of the individual steps in nitrogen adsorption on a

Fe(111) surface, which was chosen since it is the most active low-index single crystal plane of iron in nitrogen activation [2]. It will be shown that the energetics are quite similar to those found with other nitrogen/metal systems, but that unusually low preexponential factors are responsible for the unique kinetic properties.

2. Experimental

The experiments were performed with a standard UHV system equipped with facilities for LEED, AES, thermal desorption spectroscopy and work function measurements. The temperature of the sample could be varied between 120 and 1000 K by a combined cooling-heating device. Cleaning of the surface was performed as described earlier [2,3]. Dissociation of N_2 on a clean Fe(111) surface up to a small concentration (about $2 \times 10^{13} \text{ cm}^{-2}$) was found to easily take place even at the lowest attainable temperatures ($\sim 120 \text{ K}$). The measurements to be described were always performed with surfaces exhibiting this extent of dissociative adsorption.

3. Results

3.1. Molecular adsorption

Thermal desorption spectra were recorded with a heating rate of about 5 K/s after exposing the surface to N_2 at 120 K. Typical data are reproduced in fig. 1. Parameter is the corresponding change of the work function, $\Delta\phi$, which was recorded simultaneously. The maximum rate of desorption occurs at $T_{\text{max}} = 160 \text{ K}$ from which a first rough estimate on the activation energy of this process can be made: $E_d \lesssim 10 \text{ kcal/mole}$. This value is much lower than those determined for the associative desorption of atomic nitrogen (51 kcal/mole [2]). Accordingly this latter process takes place only above $\sim 700 \text{ K}$. Although no direct spectroscopic identification of the present weakly held species was possible it is quite obvious that it is molecular in nature: (i) The desorption temperature is in the same range as with the system $N_2/\text{Ni}(110)$ [8–10] or $N_2/\text{Ir}(110)$ [11], where the existence of $N_{2,\text{ad}}$ was demonstrated by means of UPS. (ii) XPS experiments with N_2 interacting with polycrystalline Fe led to the identification of molecularly adsorbed nitrogen which desorbed slowly even at 80 K [5]. (iii) TDS experiments performed after exposing the surface to a mixture of $^{28}\text{N}_2$ and $^{30}\text{N}_2$ yielded no indication for isotopic exchange, whereas complete isotopic equilibration was observed in the case of the atomic species recombining at high temperature [2].

The maximum of the TDS traces in fig. 1 is only slightly shifting with coverage which indicates first order desorption with an almost constant

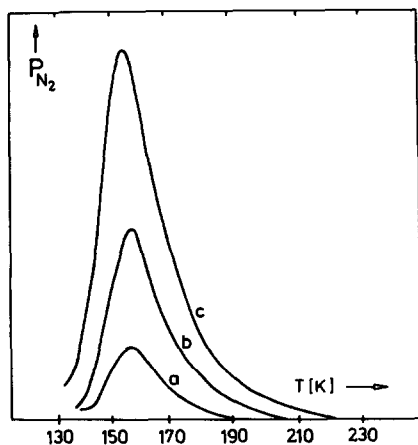


Fig. 1. Thermal desorption spectra for nitrogen molecularly adsorbed on exposure at 120 K. Heating rate 5 K/s. Parameter is the work function change $\Delta\phi$: (a) $\Delta\phi = 9$ mV, (b) $\Delta\phi = 44$ mV, (c) $\Delta\phi = 115$ mV.

activation energy. With increasing coverage desorption is, however, already taking place at the lowest attainable temperature (120 K) so that saturation of the adlayer could not be reached. The high temperature tails beyond T_{\max} are presumably partly caused by spurious effects arising from inhomogeneous heating, insufficient pumping rate etc.

Adsorption of N_2 causes a continuous increase of the work function up to about $\Delta\phi = 140$ meV. The variation of the work function with the N_2 exposure (at $p_{N_2} = 2 \times 10^{-6}$ Torr) at 120 K is reproduced in fig. 2.

Since the electron beam used for AES caused severe distortion of the N_2

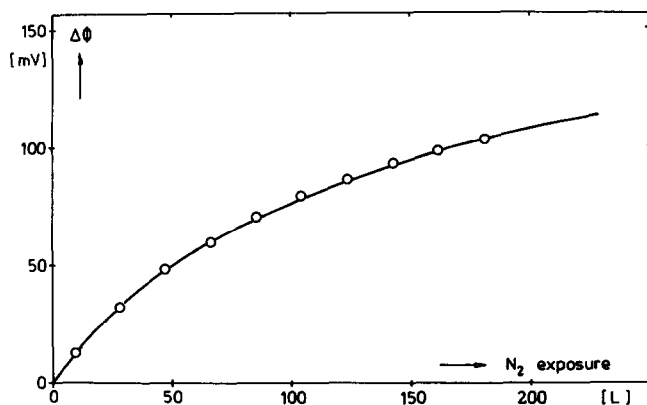


Fig. 2. Variation of the work function with N_2 exposure at 125 K ($p_{N_2} = 2 \times 10^{-6}$ Torr).

adlayer, this technique could not be used for calibration of the surface concentration. Instead this was performed by means of the areas below the thermal desorption traces:

$$[N_{2,ad}] = \alpha(AkT)^{-1} \int p_{N_2} dt. \quad (1)$$

Here, A is the surface area of the sample and α a parameter characterizing the vacuum system (being composed of the pumping speed and a geometric factor). The value of α was determined through thermal desorption of atomically adsorbed nitrogen from Fe(100) where the actual surface concentration was known from LEED/AES data [2]. Although this complex procedure introduces a rather high degree of uncertainty the resulting values appear to be reasonable: The maximum surface concentration under the present conditions results to be around $1 \times 10^{14} \text{ cm}^{-2}$. In the presence of coadsorbed potassium (which increases the N_2 adsorption energy) this value rises to about $2.5 \times 10^{14} \text{ cm}^{-2}$ [12]. This has to be compared with the number of $4.5 \times 10^{14} \text{ cm}^{-2}$ derived for Fe films at 77 K [6] or of $4.8 \times 10^{14} \text{ cm}^{-2}$ for Ir(110) saturated at 95 K [11]. Thus our calibration might be too small by about a factor of two. This, however, will be of no qualitative significance for the further discussion which will be mainly restricted to the limit of zero coverage. Comparison of the $\Delta\phi$ values with the corresponding areas below the thermal desorption traces ($\hat{=} N_{2,ad}$ concentrations) yielded a linear relation as shown in fig. 3.

Adsorption isotherms for the equilibrium $N_2 = N_{2,ad}$ in the low coverage range were recorded by using $\Delta\phi$ as a monitor for the surface concentration.

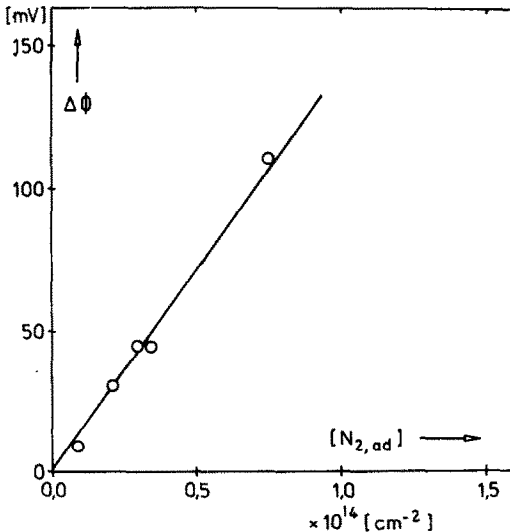


Fig. 3. Variation of the work function change $\Delta\phi$ with the surface concentration of $N_{2,ad}$.

The result is reproduced in fig. 4. (The $\Delta\phi$ values were converted into $[N_{2,ad}]$ through fig. 3.) Analysis of these data in terms of the Clausius–Clapeyron equation,

$$\left(\partial \ln p / \partial (1/T)\right)_\theta = -\Delta H_{ad}/R,$$

yields the isosteric heat of adsorption: $\Delta H_{ad} = 7.5 \pm 0.5$ kcal/mole (at low coverages) (it should be mentioned that these data were derived for surfaces with $[N_s] \approx 1 \times 10^{14}$ cm $^{-2}$).

Since there is no indication of an activation energy for the process $N_2 \rightarrow N_{2,ad}$, ΔH_{ad} may be set equal to the activation energy for desorption, E_d . This may be used to determine the pre-exponential for desorption, ν_d , from the thermal desorption spectra: In the case of first-order desorption the following relation holds

$$E_d/RT_{max}^2 = (\nu_d/b) \exp(-E_d/RT_{max}), \quad (2)$$

where b is the heating rate (5.1 K/s). Insertion of the known parameters E_d , T_{max} and b yields $\nu_d \approx 2 \times 10^{10 \pm 1}$ s $^{-1}$. This value appears to be unusually small if compared with the frequently assumed number of 10^{13} s $^{-1}$, but is by no means unique.

The slope of the coverage vs. exposure plot as shown in fig. 2 yields in principle the sticking coefficient for molecular adsorption, s . However, the TDS data indicate that even at the lowest attainable temperature (~ 120 K) the rate of desorption is not negligible, so that the thus determined s will be smaller than the true value. In this way the “apparent” initial sticking

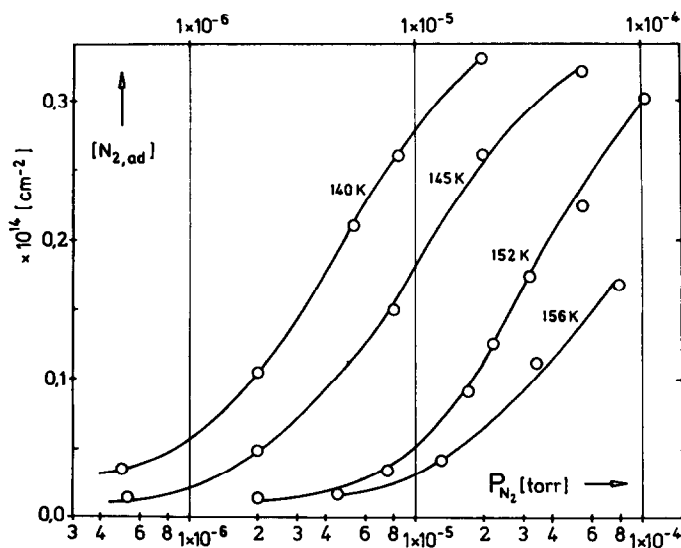


Fig. 4. Adsorption isotherms for the equilibrium $N_2 = N_{2,ad}$.

coefficient at 120 K results to be $s_0 \approx 3 \times 10^{-3}$. An upper limit for the "true" s_0 is obtained from our experiments with K-precovered Fe(111) surfaces where the N_2 molecules are more tightly bound and a (true) value of $s_0 = 6 \times 10^{-2}$ resulted [12]. It is thus concluded that for the present system $s_0 = 10^{-2 \pm 0.5}$. Despite the rather large uncertainty it is quite obvious that this quantity is considerably smaller than that for other systems of molecular adsorption where usually numbers near unity are derived. (This also holds, for example, for the systems $N_2/Ni(110)$ [8] or $N_2/Ir(110)$ [11].)

3.2. Dissociative adsorption

Although N_2 molecules adsorbed at low temperature can be thermally desorbed almost quantitatively without intermediate dissociation, in parallel a slow conversion into the atomic species, N_s , takes place. The variation of the surface concentration of N_s was followed mainly by AES after desorbing the molecularly adsorbed nitrogen and after evacuation of the vacuum system (in order to avoid spurious effects by dissociation of gaseous N_2 by the AES electron beam)*. Previous studies [2,3] have shown that atomic nitrogen may also readily dissolve in the bulk. In order to prevent interference with such effects the subsurface region was saturated with nitrogen by high N_2 exposures followed by mild argon ion sputtering and annealing of the surface prior to the experiments. Such a procedure was found in previous work [2,3] to minimize that influence of bulk effects.

The variation of the N_s concentration with N_2 exposure (at $p_{N_2} = 10^{-4}$ Torr) at different surface temperatures 214, 269 and 423 K, is reproduced in fig. 5. The initial slope (i.e. extrapolated to $[N_s] = 0$) of these curves yields the dissociative sticking coefficient, σ_0 , on a clean Fe(111) surface, i.e. the probability that a N_2 molecule striking the surface from the gas phase becomes dissociatively adsorbed from

$$d[N_s]/dt = 2\sigma dN/dt, \quad (3)$$

where $dN/dt = p_{N_2}(2\pi MRT)^{-1/2}$ is the flux of N_2 molecules striking 1 cm^2 of the surface per second. At $T_s = 423 \text{ K}$ we obtain $\sigma_0 = 5 \times 10^{-6}$ which value is in rather good agreement with the data derived in earlier work [2]. These previous investigations were only performed over a limited range of surface temperatures between 300 and 500 K, where no noticeable temperature dependence of σ_0 was recognized and therefore on an effective activation energy $E^* \approx 0$ was concluded. The present data show that σ_0 even decreases with increasing surface temperature: Analysis of the data in terms of an Arrhenius form, $\sigma_0 = \nu_\sigma \exp(-E^*/RT)$, yields $\nu_\sigma = 2.2 \times 10^{-6} \text{ s}^{-1}$ and $E^* = -0.8 \text{ kcal/mole}$. With increasing coverage, however, E^* increases continuously and soon reaches positive values.

* Conversion of the AES signal intensities into $[N_s]$ values was performed as in previous work [2].

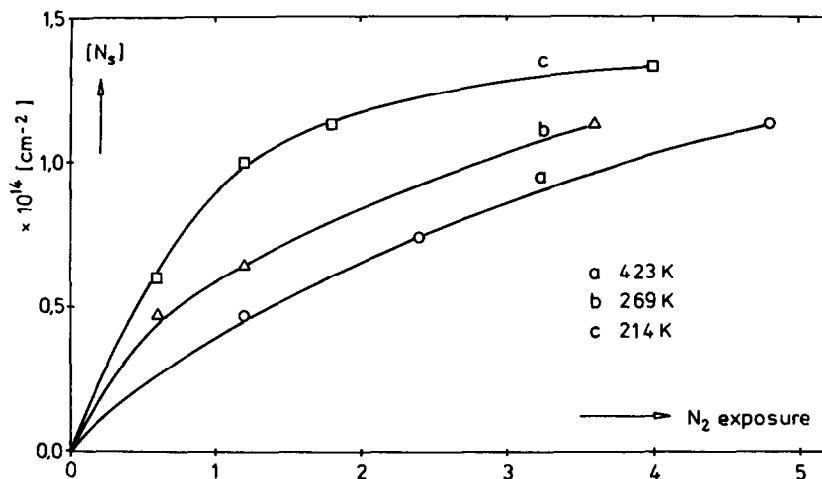


Fig. 5. Variation of the surface concentration of atomic nitrogen $[N_s]$, with N_2 exposure at three different temperatures (unit of exposure is 10^6).

Like the molecular species, atomic nitrogen causes a continuous increase of the work function. The associated dipole moment of the adsorbate complex is about 0.25 D. Since, however, atomic nitrogen causes complex reconstruction of the substrate surface interpretation is rather complicated. The LEED patterns and thermal desorption data of the atomic species observed in the present work were in complete agreement with those reported earlier [2].

4. Discussion

Molecular adsorption of nitrogen with desorption temperatures between 100 and 200 K has already been reported for a large variety of transition metals such as Ni [6–10,13–15], Fe [2,4–7], W [16–18], Pd [15], Pt [19,20], Ir [11,21], and Ru [22]. Since N_2 is isoelectronic with CO it appears to be rather plausible to assume a similar surface configuration, namely “end-on” M–N–N rather than the molecular axis lying parallel to the surface. Experimental evidence for this structure is obtained by the observation of the N–N stretch vibration in the adsorbed state (which would otherwise be dipole forbidden) [8,17,19,23,24] as well as from angular resolved photoemission [18]. This picture is supported by theoretical cluster calculations [18,25,26] which were mainly performed for interpretation of the UPS data and by which a “side-on” configuration could clearly be ruled out. Electron population analysis within a recent ab initio MO calculation [26] revealed a slight electron transfer from the transition metal atom to the N_2 ligand which reflects a “ π -backbonding” contribution to the bond formation and accounts for the observed shift of the N–N stretch

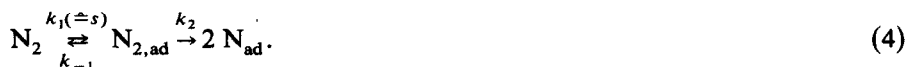
frequency (with respect to the gas phase) as well as for the increase of the work function observed in the present study giving rise to a small dipole moment (~ 0.4 D) of the adsorbed complex.

In previous work on molecular nitrogen adsorption at iron surfaces, several times a decrease rather than an increase of the work function was reported [2,27,28]. During the present experiments it turned out that the N_2 induced $\Delta\phi$ changes its sign in the presence of small amounts of coadsorbed hydrogen which is presumably the reason for this apparent discrepancy.

The present value of 7.5 kcal/mole for the heat of adsorption of N_2 on Fe(111) (at low coverages) fits well into the general experience of previous work: With evaporated Fe films Wedler et al. [6] determined a constant value of 5 kcal/mole up to $[N_{2,ad}] \approx 4 \times 10^{14} \text{ cm}^{-2}$, whereas Beeck et al. [7] determined a value of about 9 kcal/mole. Initial adsorption energies of 8.5 kcal/mole were reported for Ni(110) [8] as well as Ir(110) [11]. In the latter study the preexponential factor for desorption was found to range between 10^8 and 10^{11} s^{-1} which is also in agreement with the present value of $10^{10 \pm 1} \text{ s}^{-1}$.

The properties of the atomic species, N_s , have been extensively studied in the past with single crystal [2,3] as well as polycrystalline [19,29,30] iron surfaces. Its structure is described in terms of "surface nitride" formation which is closely related with the atomic configuration in low-index planes of (bulk) Fe_4N [2,3]. There is general agreement that the overall sticking coefficient for the process $N_2 \rightarrow 2N_s$ depends on the surface structure and lies in the range of 10^{-7} to 10^{-6} , although the apparent activation energy is rather small [2,3,30]. Recent work by Wedler et al. [30] with evaporated Fe films revealed in some cases even slightly negative values (~ -0.2 kcal/mole) for this quantity which supports the present findings with Fe(111).

The kinetics of dissociative nitrogen chemisorption is formulated in terms of the following sequence of reaction steps:



The following discussion will be restricted to the limit of zero coverage so that the influence of the surface concentration of adsorbed species can be neglected. That molecularly adsorbed N_2 is the "precursor" for dissociative adsorption, has already been concluded in earlier work [2-5,27,30]. A "direct" mechanism $N_2 \rightarrow 2 N_{ad}$ appears to be rather improbable for the following reasons:

(i) $N_{2,ad}$ is slowly converted into N_s even at 80 K without N_2 in the gas phase, as followed by XPS [5].

(ii) The overall sticking coefficient for dissociative adsorption, σ_0 , is smaller by several orders of magnitude than that for trapping into the molecular state, s_0 .

If the direct mechanism would prevail the channel $N_{2,ad} \xrightarrow{k_2} 2 N_{ad}$ should be practically closed which would be in contradiction to the observations of Johnson and Roberts [5]. In addition experiments with a molecular beam

revealed no evidence for an increase of σ_0 with increasing translational energy of the N_2 molecules [31]. This would be expected if an activation barrier is "directly" surmounted as for example observed with the system H_2/Cu [32]. (iii) Thorman et al. [33] investigated the occupation of the vibrational states of N_2 molecules formed by association of nitrogen atoms which were diffusing through a polycrystalline iron foil and found that this obeyed thermal equilibrium at the surface temperature, provided that the surface was clean. Vibrationally "hot" N_2 molecules were only detected if the surface was covered by sulfur which element is known to inhibit nitrogen adsorption. Since the reverse step has to proceed through the same microscopic states, these results therefore also strongly support the view that molecularly adsorbed and thermally equilibrated N_2 forms the intermediate in dissociative adsorption.

The derivation of the kinetic parameters is illustrated by the Lennard-Jones type potential diagram as shown in fig. 6 and is related to the scheme as proposed by Wedler et al. [30]:

(a) The rate of adsorption into the molecular state is given by

$$d[N_{2,ad}]/dt = k_1 p_{N_2} = s_0 p_{N_2} (2\pi MRT)^{-1/2}. \quad (5)$$

Thus k_1 is proportional to the sticking coefficient s_0 for which at 120 K a value $s_0 = 10^{-2 \pm 0.5}$ was derived. The temperature dependence of this quantity is not yet known, but is assumed to be negligible over the range under discussion (which, however, might be a matter of dispute).

(b) The rate of desorption from the molecular state can be written as

$$-d[N_{2,ad}]/dt = k_{-1} [N_{2,ad}], \quad (6)$$

where k_{-1} ($=k_d$) $= \nu_{-1} \exp(-E_1/RT)$. The parameters ν_{-1} ($=\nu_d$) and E_1 ($=E_d$) have been determined as $\nu_{-1} = 10^{10 \pm 1} \text{ s}^{-1}$, $E_1 = 7.5 \pm 1 \text{ kcal/mole}$.

(c) The rate of dissociative adsorption is given by

$$d[N_s]/dt = k_2 [N_{2,ad}] = 2\sigma_0 p_{N_2} (2\pi MRT)^{-1/2}. \quad (7)$$

The overall sticking coefficient for dissociative adsorption is given by $\sigma_0 = \nu_\sigma \exp(-E^*/RT)$, where $\nu_\sigma = 2.2 \times 10^{-6}$ and the apparent activation energy $E^* = -0.8 \text{ kcal/mole}$ were determined experimentally. In order to derive $k_2 = \nu_2 \exp(-E_2/RT)$ from the experimental σ_0 and the other available data it is assumed that $[N_{2,ad}]$ is determined through the equilibrium $N_2 \rightleftharpoons N_{2,ad}$ [30]. This assumption is safely justified since experimental experience demonstrated that the rate of desorption of $N_{2,ad}$ exceeds much that for dissociation, i.e. $k_{-1} \gg k_2$.

At equilibrium eqs. (5) and (6) are equal and yield

$$[N_{2,ad}] = (s_0/k_{-1}) p_{N_2} (2\pi MRT)^{-1/2}, \quad (8)$$

from which by combination with eq. (7) we obtain

$$k_2 = 2\sigma_0 k_{-1}/s_0. \quad (9)$$

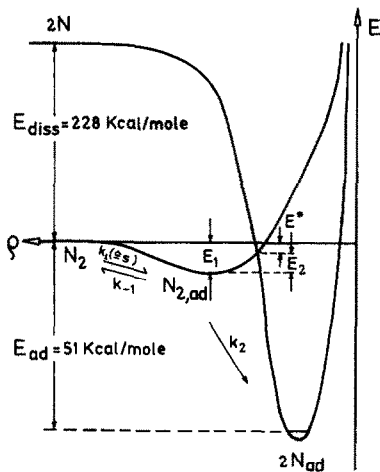


Fig. 6. Potential diagram illustrating the energetics of the individual reaction steps in dissociative nitrogen adsorption.

At 120 K, $s_0 = 10^{-2}$ and $\sigma_0 = 6 \times 10^{-5}$ (extrapolated to this temperature) which leads to $k_2/k_{-1} \approx 10^{-2}$. That means that at this temperature the rate of desorption of $N_{2,ad}$ is faster by about two orders of magnitude than that for dissociation of this species. If we assume that s_0 is independent of temperature over the range under discussion it becomes evident that this effect is caused by a striking difference between the pre-exponentials ν_{-1} and ν_2 of these two steps. Eq. (9) then writes

$$\nu_2 \exp(-E_2/RT) = 2\nu_\sigma s_0^{-1} \exp(-E^*/RT) \nu_{-1} \exp(-E_1/RT). \quad (10)$$

In this case it becomes evident that the apparent activation energy E^* is equal to the difference $E_2 - E_1$ as illustrated by fig. 6, i.e. $E_2 = E_1 + E^* = 7.5 - 0.8 = 6.7$ kcal/mole. The pre-exponentials are then related through

$$\nu_2 = 2\nu_\sigma \nu_{-1} s_0^{-1}, \quad (11)$$

yielding $\nu_2 \approx 5 \times 10^{-4 \pm 0.5} \nu_{-1} \approx 10^7 \text{ s}^{-1}$. If we return to eq. (9) which can also be written as

$$\sigma_0 = \frac{1}{2} s_0 k_2 / k_{-1} = \frac{1}{2} s_0 (\nu_2 / \nu_{-1}) \exp(-E^*/RT),$$

it now becomes obvious that the extremely small effective sticking coefficient for dissociation is determined by two factors: (i) The trapping probability for molecular nitrogen ($s_0 = 10^{-2}$) is about two orders of magnitude smaller than that usually found for molecular adsorption. (ii) The ratio ν_2/ν_{-1} ($\approx 10^{-4}$) disfavours dissociation of an adsorbed N_2 molecule extremely against thermal desorption. Both factors account for the fact that (apart from the existence of an "apparent" activation energy E^*) dissociative adsorption of nitrogen takes

place with a rate which is smaller by a factor of about 10^6 than that expected on the basis of a simple collision model. This latter conclusion was already reached in 1934 by Emmett and Brunauer [34] in their study of the kinetics of nitrogen uptake by an industrial Fe ammonia catalyst.

So far these unusual kinetic features appear to be unique for the N_2/Fe system: With Ni(110) the strength of the M–N bond as well as the adsorption energy for molecular nitrogen are similar to the values found with iron, and also the dissociative sticking coefficient is extremely small, $\sigma_0 \lesssim 10^{-7}$ (which, however, might be affected by the existence of a noticeable apparent activation energy E^*). However the trapping probability for molecular nitrogen, s_0 , appears to be near unity with this system [8] as well as for $N_2/Ir(110)$ [11]. On the other hand, dissociative adsorption on tungsten surface takes place with probabilities up to $\sigma_0 = 0.7$, whereby, however, the adsorption energy is around 80 kcal/mole [36,37] and thus much higher than for Fe (~ 50 kcal/mole [2,3]). It has thus to be concluded that the detailed shape of the interaction potential (and not only its maxima and minima) as well as the elementary excitations of the solid surface enabling energy transfer are ultimately responsible for the peculiar overall kinetics of one of the most important catalytic reactions.

Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 128) is gratefully acknowledged.

References

- [1] G. Ertl, *Catalysis Rev.* 21 (1980) 201.
- [2] F. Bozso, G. Ertl, M. Grunze and M. Weiss, *J. Catalysis* 49 (1977) 18.
- [3] F. Bozso, G. Ertl and M. Weiss, *J. Catalysis* 50 (1977) 519.
- [4] K. Kishi and M.W. Roberts, *Surface Sci.* 62 (1977) 252.
- [5] D.W. Johnson and M.W. Roberts, *Surface Sci.* 87 (1979) 1255.
- [6] G. Wedler, D. Borgmann and K.P. Geuss, *Surface Sci.* 47 (1975) 592.
- [7] O. Beeck, W.A. Cole and A. Wheeler, *Disc. Faraday Soc.* 52 (1956) 86.
- [8] M. Grunze, R.K. Driscoll, G.N. Burland, J.C.L. Cornish and J. Pritchard, *Surface Sci.* 89 (1979) 381.
- [9] M. Golze, M. Grunze, R.K. Driscoll and W. Hirsch, *Appl. Surface Sci.*, in press.
- [10] M. Grunze, personal communication.
- [11] D.E. Ibbotson, T.S. Wittrig and W.H. Weinberg, to be published.
- [12] G. Ertl, S.B. Lee and M. Weiss, *Surface Sci.* 114 (1982) 527.
- [13] C.R. Brundle, *J. Vacuum Sci. Technol.* 13 (1976) 301.
- [14] C.R. Brundle and A.F. Carley, *Disc. Faraday Soc.* 60 (1975) 51.
- [15] D.A. King, *Surface Sci.* 9 (1968) 375.
- [16] J.C. Fuggle and D. Menzel, *Surface Sci.* 79 (1979) 1.
- [17] W. Ho, R.F. Willis and E.W. Plummer, *Surface Sci.* 95 (1980) 171.
- [18] E. Umbach, A. Schichl and D. Menzel, *Solid State Commun.* 36 (1980) 93.

- [19] R.A. Shigeishi and D.A. King, *Surface Sci.* 62 (1977) 379.
- [20] M. Wilf and P.T. Dawson, *Surface Sci.* 60 (1976) 561.
- [21] B.E. Nieuwenhuys, D.T. Meijer and W.M.A. Sachtler, *Surface Sci.* 40 (1973) 125.
- [22] R. Klein and A. Shih, *Surface Sci.* 69 (1977) 403.
- [23] R.P. Eischens and J. Jacknow, in: *Proc. 3rd Intern. Congr. on Catalysis* (North-Holland, Amsterdam, 1965) p. 627.
- [24] R.A. van Hardeveld and A. van Montfoort, *Surface Sci.* 4 (1966) 396; 17 (1969) 90.
- [25] P.A. Bagus, C.R. Brundle, K. Hermann and D. Menzel, *J. Electron Spectrosc.* 20 (1980) 253.
- [26] H. Itoh, G. Ertl and A.B. Kunz, *Chem. Phys.* 59 (1981) 149.
- [27] V. Ponec and Z. Knor, *J. Catalysis* 10 (1968) 73.
- [28] P.M. Gundry, J. Haber and F.C. Tompkins, *J. Catalysis* 1 (1962) 363.
- [29] I.D. Gay, M. Textor, R. Mason and Y. Iwasawa, *Proc. Roy. Soc. (London)* A356 (1977) 25.
- [30] G. Wedler, G. Steidl and D. Borgmann, *Surface Sci.* 100 (1980) 507.
- [31] T. Engel, *personal communication*.
- [32] R.M. Balooch, M.J. Cardillo, D.R. Miller and R.E. Stickney, *Surface Sci.* 46 (1974) 358.
- [33] R.P. Thorman, D. Anderson and S.L. Bernasek, *Phys. Rev. Letters* 44 (1980) 743.
- [34] P.H. Emmett and S. Brunauer, *J. Am. Chem. Soc.* 56 (1934) 35.
- [35] S.P. Singh-Boparai, M. Bowker and D.A. King, *Surface Sci.* 53 (1975) 55.
- [36] L.R. Clavenna and L.D. Schmidt, *Surface Sci.* 33 (1970) 365.
- [37] T.E. Madey and J.T. Yates, *J. Chem. Phys.* 43 (1965) 1055; 44 (1966) 1675.