Surface Science 257 (1991) 86–96 North-Holland

Adsorption and decomposition of hydrazine on Pd(100)

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Received 28 March 1991; accepted for publication 6 May 1991

The adsorption and decomposition of N_2H_4 on Pd(100) has been studied by measuring the sticking coefficient and by thermal desorption spectroscopy. Well-defined molecular beam dosing has been employed to limit the interaction of hydrazine to the palladium surface. Desorption of ammonia and hydrazine occurred at peak temperatures between 380 and 420 K. From the adsorption isosteres binding energies of (360 ± 50) meV and (190 ± 40) meV could be derived for NH₃ and N₂H₄, respectively. Low pre-exponential factors of $\nu_0(NH_3) = 10^{(1.1 \pm 0.5)} \text{ s}^{-1}$ and $\nu_0(N_2H_4) = 10^{(2.8 \pm 0.4)} \text{ s}^{-1}$ were found. Nitrogen and hydrogen desorption was not detected which allows identification of the relevant surface reactions leading to hydrazine decomposition.

1. Introduction

The interaction of hydrazine with metal surfaces is known to lead to inert as well as to reactive final products, i.e., nitrogen, hydrogen and ammonia. These species are formed in surface reactions proceeding via intermediate NH, radicals. The products obtained in the catalytic decomposition of hydrazine are used, e.g., as propellants for satellite rocket engines, which indicates that they may emerge from surface reactions with high kinetic energy. Despite these interesting phenomena and the possibility of generating either homonuclear diatomic or polyatomic products from the same source molecule, the basic kinetic and dynamic behaviour of hydrazine on single-crystal metal surfaces has rarely been studied in the past. The most detailed investigations were performed on Fe(111) [1], Ir(111) [2], and Rh(100) [3] surfaces. Other groups studied the interaction with supported catalytic metal surfaces and other substrates [4].

For the single-crystal surfaces studied, dissociative adsorption has been observed. Depending on the specific reaction products formed, the overall energy release may be estimated to amount to [6]

$$N_2H_4(g) \rightarrow \text{adsorbates} \rightarrow N_2(g) + 2H_2(g),$$

$$\Delta H = -22.3 \text{ kcal/mol}, \qquad (1a)$$

 $3N_2H_4(g) \rightarrow adsorbates \rightarrow 4NH_3(g) + N_2(g),$

$$\Delta H = -44.9 \text{ kcal/mol.} \tag{1b}$$

The three products $-H_2$, N_2 , and NH_3 – have accordingly been observed in two different reactions catalyzed on rhodium [3] and iridium [5] surfaces. On the surface, the highly exothermic gas-phase reaction of hydrazine with one of its decomposition products, H_2 ,

$$N_2H_4(g) + H_2(g) \rightarrow 2NH_3(g),$$

$$\Delta H = -44 \text{ kcal/mol}, \qquad (1c)$$

does not occur. The products formed in surface catalyzed reactions are determined by te energetics on the substrate at branching points for specific reaction pathways. After adsorption of hydrazine the primary step is the decomposition into various possible radical channels. For palla-

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dium these primary decomposition reactions show considerably different energetic behaviour:

$$N_{2}H_{4}(ad) \rightarrow N_{2}H_{2}(ad) + 2H(ad),$$

$$\Delta H = +3 \text{ kcal/mol } [1,7,8], \qquad (2a)$$

$$\rightarrow \text{NH}(ad) + \text{NH}_{3}(ad),$$

$$\Delta H = -40 \text{ to } -45 \text{ kcal/mol } [6,9,10], \qquad (2b)$$

$$\rightarrow 2\text{NH}_{2}(ad),$$

$$\Delta H = -46 \text{ kcal/mol } [6,10]. \qquad (2c)$$

It is obvious that the endothermic reaction (2a) is not likely to occur due to the competition from reactions (2b) and (2c). The reaction (2a) would subsequently produce predominantly molecular nitrogen and hydrogen. This pathway, corresponding to the gas-phase reaction (1a), is thus not expected to take place on the Pd(100) surface. Depending on the binding energies of NH and NH₂ to Pd, reaction (2c) would be more or less favoured over (2b). The next step after decomposition according to (2c) might be the bimolecular reaction

$$NH_2(ad) + NH_2(ad) \rightarrow NH_3(ad) + NH(ad),$$

$$\Delta H = +6 \text{ to } +1 \text{ kcal/mol } [9,10], \qquad (2c')$$

thus yielding the same products as (2b). Alternatively, after forming the amine radicals (2c) the surface reactions may proceed along an atomic pathway according to

$$3N_2H_4(ad) \rightarrow 4NH_2(ad) + 2N(ad) + 4H(ad),$$

$$\Delta H = -60 \text{ kcal/mol [6-11]} \qquad (2d)$$

$$\rightarrow 4NH_3(ad) + N_2(ad),$$

$$\Delta H = +11 \text{ kcal/mol [7-12]} \qquad (2d')$$

Although in this reaction (2d/2d') energy of about 49 kcal/mol is gained, thus slightly more than in reactions (2b) or (2c), it requires the mobility of ten atomic and molecular species on the surface. It can thus be imagined that the unimolecular decomposition process (2b) or the bimolecular reaction (2c') would occur with higher probability despite being energetically slightly less favourable due to dynamic constraints in the reaction (2d/2d'). As a first step towards an understanding of the complex reaction behaviour we report in this paper results of a mass spectroscopic study of the sticking coefficient and the desorption kinetics of hydrazine and its products from a Pd(100) surface.

2. Experimental

The experiments are performed in an ultrahigh vacuum chamber (base pressure 6×10^{-11} mbar) equipped with LEED/Auger instruments and a quadrupole mass spectrometer (QMS). The Pd(100) crystal is mounted on a manipulator in a concentric oven which provides radiative heating up to 1000 K, with the lowest T_s given by room temperature. The crystal temperature is monitored by a Ni–NiCr thermocouple spot-welded to its circumference. The main contaminant of the surface is sulfur, which segregates at high temperatures (> 500 K) from the bulk. The sulfur is removed by brief low-voltage (500 eV) Ar⁺ ion bombardment.

Hydrazine is supplied to the surface by a pulsed, double differentially pumped molecular beam doser. This method ensures that only the Pd(100) crystal surface is dosed with hydrazine molecules. The molecular beam is formed by expanding pure hydrazine or a N_2H_4 /He mixture through a pulsed nozzle with a 500 μ m diameter opening. The pulse length can be varied between 400 μ s and 4 ms, with about 1 ms employed in the experiment. The beam divergence is determined to be about 1° after double skimming. resulting in a spot diameter of about 2.5 mm on the 10 mm diameter crystal. With a supply pressure of 95 mbar hydrazine at the nozzle, a repetition rate of 1 Hz, and a pulse length of 1 ms, the averaged hydrazine flux is 3.9×10^{14} cm⁻²s⁻¹, with a peak flux of 3.9×10^{17} cm⁻²s⁻¹. For the thermal desorption spectra the crystal is dosed with different pre-set numbers of gas pulses. When pure He is used the pulsed molecular beam can be used to check the smoothness of the crystal surface. Because the QMS is positioned at a right angle to the molecular beam source, it is possible to measure the angular distribution of the scattered He atoms by rotating the crystal. In addition, the pulsed expansion allows the use of a comparatively large expansion parameter $(p_0 d)$

of about 5 mbar cm, where p_0 is the stagnation pressure and d is the nozzle diameter. A large value of (p_0d) results in a well-defined kinetic energy distribution of the He beam. This velocity distribution is given by [14]

$$f(v) = c \left(\frac{v}{v_{\rm s}}\right)^3 \exp\left[-\frac{\gamma}{2} \left(\frac{v}{v_{\rm s}} - 1\right)^2 M_{\rm t}^2\right],\qquad(3)$$

where c is a normalization constant, $\gamma = c_p/c_v$ the ratio of the specific heat capacities, M_t the terminal Mach number, and v_s the stream velocity

$$v_{\rm s}^2 = \frac{2kT_0}{m} \frac{\gamma}{2} M_t^2 \left(1 + \frac{\gamma - 1}{2} M_t^2 \right)^{-1}$$
(4)

For the given expansion conditions, an average velocity of 1693 m s⁻¹ for a pure He beam is calculated. The velocity spread amounts to $\Delta v / v$ = 12% (FWHM). The scattering He atoms therefore have an incident energy of $E_i = (63 \pm 13)$ meV. Similarly, for a pure N₂H₄ beam one arrives at a kinetic energy of $E_i = (107 \pm 38) \text{ meV}$ (backing pressure 95 mbar). For the hydrazine seeded in He this kinetic energy increases to $E_1 = (442 \pm 110)$ meV, when 3% N₂H₄ is expanded in 100 mbar He. For a clean Pd(100) surface at $T_s = 295$ K a relatively narrow angular distribution ($\Delta \Theta \sim 10^{\circ}$) is obtained, which is determined in part by the angular spread of the incident beam and that of the detecting aperture in the QMS. When S atoms are present on the surface this angular distribution broadens significantly to about $\Delta \Theta \sim 18^{\circ}$ (FWHM).

Hydrazine is prepared and stored in a glass manifold. The commercial hydrazine anhydride (Roth, stated purity: 98%) is purified by a standard freeze-thaw technique, and then stored at liquid nitrogen temperature. Just before use, it is evaporated into a large glass vessel. This storage vessel, together with the whole supply manifold to the nozzle, can be heated to achieve the required pressures for the expansion, because N_2H_4 has a vapour pressure of only 13 mbar at 20°C.

In the quadrupole mass analyzer, hydrazine appears not only on the parent mass 32 amu, but also at different fragment masses, notably at 28 amu (N_2), 17 amu (NH_3), and masses 14 to 16 amu and 29 to 31 amu. Some products expected from surface reactions, e.g., N_2 and NH_3 , and common background gases, CO and H_2O , also show up at these masses. Therefore, a careful analysis of the QMS cracking pattern of hydrazine and ammonia has been carried out. These data are shown in table 1, together with those of other gases taken from the literature.

Sticking coefficients have been determined only after a mild overnight bake-out of the chamber, in order to operate at a reduced partial pressure of water. Before a measurement of the sticking coefficient is performed, the crystal is removed from the molecular beam path, and the chamber walls are equilibrated with hydrazine for a few minutes. This procedure was necessary because we found that initially clean chamber walls pump hydrazine very efficiently, although with changing pumping speed depending upon the degree of saturation. Due to this wall effect the standard

Table 1 Cracking pattern of hydrazine and other relevant gases

	Mass number (amu)												Ref.
	1	2	14	15	16	17	18	28	29	39	31	32	
$\overline{N_2H_4}$			6.9	9.1	38.3	56.2	18.1	84.8	53.5	32.0	45.9	100	This work
NH ₃		3.4	8.9	7.1	76.1	100		48.6		11.1			[15]
N_2			20.0						100				[15]
H_2	2.0	100											[15]
H ₂ O					1.8	21.5	100						[15]
0 ₂					13.5							100	[15]

method of measuring an increase of the partial pressure upon dosing was unreliable. In our approach, when the admittance of hydrazine to the chamber is blocked, an exponential decrease of the hydrazine partial pressure with a time constant of about 75 s due to the desorption from the chamber walls is observed. The same comparatively slow partial pressure drop occurs at the beginning of a sticking coefficient measurement, and thus the partial pressure has to be extrapolated back to t_0 to obtain S_0 (see fig. 1). The average total chamber pressure at the beginning of an adsorption run is about 1×10^{-10} mbar. For the measurement of the sticking coefficient the crystal is dosed at 295 K, for TDS data dosing occurred at about 325 K. The thermal desorption spectra are obtained by supplying constant power to the radiatively heating oven, yielding over most part of the temperature range a constant heating rate of the crystal of about $\beta = 0.6 \text{ K s}^{-1}$. Only in the beginning of a TDS run (up to 393 K) is a deviation from the constant heating rate observed. However, it is small and very reproducible from run to run. The temperature dependent heating rate $\beta(T)$ can thus safely be taken into account in the analysis of the spectra.

3. Results

3.1. Hydrazine sticking

Adsorption experiments are carried out after pre-dosing the chamber walls until an equilibrium partial pressure of hydrazine of about 7×10^{-11} mbar in the chamber is reached. During operation of the seeded molecular beam at 3 Hz repetition rate, the total pressure is the chamber increases to 1.3×10^{-10} mbar. Between two consecutive molecular beam pulses the palladium surface is brought into the beam path and the surface exposed to hydrazine. During this time the N_2H_4 partial pressure is monitored. Fig. 1 shows a typical trace of the mass 32 signal. At t_0 the Pd(100) surface is moved into the N_2H_4/He dosing beam, and the measured N_2H_4 partial pressure drops by about 2.5×10^{-12} mbar. The initial drop due to adsorption on the Pd(100) crystal is partially obscured by hydrazine desorbing from the chamber walls, as outlined in the experimental section. To obtain S_0 , the pressure curve is therefore extrapolated back to t_0 . At a N₂H₄ flux of 4.5×10^{12} cm⁻²s⁻¹ within the molecular beam, the hydrazine partial pressure



Fig. 1. Partial pressure change of N_2H_4 after moving at t_0 the Pd(100) surface between consecutive molecular beam pulses into the molecular beam. The slow decrease of the partial pressure after t_0 is due to hydrazine release from the chamber walls. The solid curve indicates the pressure extrapolation to t_0 (see text).

returns to its old value within about 7 min. In fig. 1 the kinetic energy of the N_2H_4 molecules is about (422 ± 110) meV. Without seeding, no pressure drop is discernible at the given level of sensitivity.

According to King and Wells [16] the sticking coefficient S(t) is obtained from

$$S(t) = \frac{P(t_0) - p(t)}{p(t_0)},$$
(5)

where $p(t_0) - p(t) = \Delta p$ is the pressure difference at a certain time $(t - t_0)$ after exposing the crystal surface to the molecular beam. The method permits the determination of the initial sticking coefficient S_0 without knowledge of the incoming molecular flux Q. When this flux Q is known and the pumping speed is high enough so that the flux density may be taken to be directly proportional to the partial pressure, the sticking coefficient S can be derived as a function of the coverage $\theta(t)$

$$\theta(t) = Q \int_{t_0}^t S(t') \, \mathrm{d}t'. \tag{6}$$

Using this procedure we arrive at an initial sticking coefficient of N₂H₄ on Pd(100) of $S_0 = 0.37 \pm 0.05$ for a kinetic energy of the hydrazine molecules of (442 ± 110) meV.

Fig. 2 shows the sticking coefficient as a function of surface coverage. A saturation coverage of 0.27 ± 0.15 ML is obtained. At two coverages typical error bars are given. A bimodal dependence can be noticed, although the comparatively large error bars do not permit the conclusion that two kinds of adsorbed species are involved in this process from the adsorption measurement alone. A search for a hydrazine induced LEED structure at $T_s \sim 300$ K was not successful. For hydrazine molecules with low kinetic energies (107 meV), a decrease of the mass 32 (amu) partial pressure cannot be observed, setting an upper limit for the initial sticking coefficient of $S_0 < 0.05$ for a signal-to-noise ratio of one. This behaviour suggests that a barrier exists for direct adsorption of N_2H_4 on Pd(100). It should be noted, however, that dosing the surface with this low-energy hydrazine eventually leads to adsorption and thus to sticking. In this case the same TDS spectra and



Fig. 2. Sticking coefficient of hydrazine as a function of surface coverage: $S_0 = (0.37 \pm 0.05)$. Two typical error bars are shown. The dashed line indicates a fit for direct chemisorption, the solid line just guides the eye.

the same relative yields are obtained as for dosing with high kinetic energy molecules. During the adsorption of hydrazine at $T_s = 295$ K the release of ammonia into the gas phase is observed. The maximum of this desorption occurs about 1 min after t_0 , indicating that a surface reaction is involved. Other desorbing molecules, e.g., H₂, are not observed.

3.2. Thermal desorption

In thermal desorption spectroscopy signals are detected only at masses 14, 16, 17, 28 and 32 amu. The observation that the peak height of the mass 17 amu signal is ten times as high as that of mass 32 amu, together with the fragmentation pattern given in table 1, leads to the conclusion that only NH_3 and N_2H_4 molecules desorb from the surface. In particular, the desorption on N_{2} can be excluded, and no desorption signal associated with H₂ is observed. Integrating the desorption fluxes of NH_3 and N_2H_4 , the number of adsorbed molecules are obtained to within 30% uncertainty. Fig. 3 shows thermal desorption spectra of NH₃ after exposing the Pd(100) surface at $T_s \sim 325$ K to hydrazine with different numbers of molecular beam pulses. At low dosage a peak desorption temperature of $T_p(NH_3) =$ 420 K is observed, which slightly decreases to $T_{\rm p} = 400 \text{ K}$ at high exposure. A plot of the isothermal desorption rates between 340 and 460 K yields slopes of 1.34 ± 0.35 . A mainly first-order desorption process is thus observed, but a contribution from a second order process must also be considered. The isosteric desorption rates are shown in fig. 4a. From the slopes of this figure, an average desorption energy for NH₃ from Pd(100) of $E_{des} = (360 \pm 50)$ meV is obtained. This desorption energy does not show a significant dependence on the surface coverage (fig. 6a).

For hydrazine (32 amu) desorption a peak maximum at $T_p = 400$ K is observed at low dosage which also shifts slightly to $T_p = 380$ K at high dosage. Fig. 5 shows the isothermal desorption rates for hydrazine. These rates yield average slopes of (1.08 \pm 0.12), indicating thus a first-order desorption kinetic. From the isosteric desorption



Fig. 3. TPD spectra of ammonia after dosing the Pd(100) surface with different amount of hydrazine; (a) 4000, (b) 3000, (c) 2000, (d) 1000, (e) 500 pulses. 1×10^{12} molecules per pulse.

rates (fig. 4b) an average desorption energy of $E_{des} = (190 \pm 40) \text{ meV}$ is derived. A dependence of the desorption energy upon the surface coverage can also in this case not be observed within the error bars (fig. 6b).

The determination of the pre-exponential factors $\nu_0(\theta \to 0)$ from the isosteric desorption rates according to ref. [17] is naturally associated with comparatively large errors. Using this method we arrive for hydrazine at $\nu_0(\theta = 0) = 10^{(1.1 \pm 0.5)} \text{ s}^{-1}$, and for ammonia at $\nu_0(\theta = 0) = 10^{(2.8 \pm 0.4)} \text{ s}^{-1}$. These very low pre-exponential factors suggest the existence of constraints for the molecular desorption pathway. A similarly low ν_0 was observed for ammonia desorption from a hydrazine-dosed Ir surface [18].

4. Discussion

At high kinetic energies of the incoming molecules, we are able to observe the sticking coefficient directly using the King and Wells method. A similar observation is not possible for N_2H_4 with low kinetic energy, although in this case it is also possible to adsorb hydrazine molecules. This suggests the existence of a barrier against direct chemisorption. In addition, the bimodal dependence of the sticking coefficient on the coverage suggests the occupation of different adsorption sites and/or the existence of different species on the surface. It seems likely that at low coverages and high kinetic energies direct chemisorption is favoured. However, the quality of the data does not permit a definite distinction between a direct chemisorption mechanism and an intrinsic precursor-mediated adsorption at low coverages. Such a precursor-mediated pathway for adsorption is likely to be existent. This can be concluded from the observation of hydrazine de-



Fig. 4. (a) Isosteric desorption rates for NH₃. A desorption energy of $E_{des} = (360 \pm 50)$ meV is derived. (b) Isosteric desorption rates for N₂H₄. A desorption energy of $E_{des} = (190 \pm 40)$ meV is obtained.



Fig. 5. Isothermal desorption rates for hydrazine desorption from Pd(100); slope: 1.08 ± 0.12 .

sorption after dosing the crystal at low kinetic energies, where a direct determination of the sticking coefficient was not possible, but TDS spectra have been observed. Moreover, it is even likely that the same species are formed at the surface from both high and low kinetic energy dosing, since in both cases identical TDS spectra are observed.

The two species observed in desorption, NH₃ and N₂H₄, both show a nearly first-order desorption kinetic. Hydrazine thus adsorbs molecularly and dissociatively on Pd(100). A first-order desorption kinetic of hydrazine has also been observed from a Rh(100) surface at $T_s = 220$ K [3]. However, the desorption energy of 560 meV, at which the authors arrived by assuming a usual pre-exponential factor of $\nu_0 = 10^{13}$ s⁻¹, is considerably higher than the value of 190 meV derived from this experiment. From other metallic surfaces N₂H₄ desorption has not been observed.

The weak release of ammonia during the adsorption is observed only after an induction period, suggesting that a bimolecular reaction is required. The TDS spectra for NH_3 then only show a high-temperature feature of ammonia, which is comparatively tightly bound to the surface. The existence of a less tightly bound ammonia species, which would desorb below room temperature, cannot be tested in the present apparatus. On Rh(100) ammonia desorption was observed at 150 and 270 K [3], whereas from Ir the desorption peak occurs at 400 K [5,18], a temperature similar to the desorption temperature observed in this work. The desorption energy of 460 meV for NH₃ from iridium [18] is also similar to the present value for a palladium surface. For rhodium this value has not been determined.

Regarding the chemistry involved in forming the observed products, the interpretation is directed by the absence of N_2 and H_2 in the desorption flux. As pointed out already in section 1 the endothermic reaction (2a), which subsequently would lead to molecular nitrogen and hydrogen, is not favoured due to the competition from the highly exothermic reactions (2b) and (2c). The pathway (2c) yields two radicals per hydrazine molecule which will undergo further surface reactions. Stable products are formed



Fig. 6. (a) Desorption energy for NH₃ as a function of surface coverage, yielding a coverage independent value of (360 ± 50) meV. (b) Desorption energy for N₂H₄ at different surface coverages, yielding an average value of (190 ± 40) meV.

when one of these radicals decomposes to its atomic constituents, viz.

$$6NH_2(ad) \rightarrow 4NH_2(ad) + 2N(ad) + 4H(ad),$$

$$\Delta H = -13.9 \text{ kcal/mol}, \qquad (2d'')$$

where these atoms react further to yield

$$\rightarrow 4\text{NH}_3(\text{ad}) + \text{N}_2(\text{ad}),$$

$$\Delta H = +17.7 \text{ kcal/mol.} \qquad (2\text{d}')$$

This atomic channel is thus endothermic by about 4 kcal/mol. In addition it involves the reaction of ten absorbed particles and the somewhat arbitrary disintegration of only two amine radicals.

This reaction pathway yielding N_2 is thus not favoured from an energetic nor from a dynamic point of view, in accordance with the experiment. If the decomposition of NH_2 proceeds only into NH + H, subsequent reaction of the released H atom with a second NH_2 yields ammonia and NH radicals:

$$2NH_{2}(ad) \rightarrow NH_{2}(ad) + NH(ad) + H(ad),$$

$$\Delta H = -5.6 \text{ to } -0.6 \text{ kcal/mol} [8-10] \quad (7a)$$

$$\rightarrow NH_{3}(ad) + NH(ad),$$

$$\Delta H = +6.6 \text{ kcal/mol} [8-10]. \quad (7b)$$

This reaction is endothermic by +1 to +6 kcal/mol, depending of the binding energy of NH on Pd [10]. If we take the same binding energy of the NH radical to Pd(100) as it is measured for a Fe substrate ($\Delta H = -100$ kcal/mol) [1], the reaction sequence (7) is exothermic by $\Delta H = -24$ kcal/mol. The ammonia formed in this reaction can easily desorb ($\Delta H = +8$ kcal/mol) in a second-order desorption kinetic. The imine radical, however, will stick at the surface. The same products are formed in a direct reaction between two amine radicals, as already mentioned in the introduction:

$$2\text{NH}_2(\text{ad}) \rightarrow \text{NH}_3(\text{ad}) + \text{NH}(\text{ad}),$$
$$\Delta H = +1 \text{ to } +6 \text{ kcal/mol [9,10]}.$$
(7c or 2c')

Also in this reaction to ammonia desorbs in a second-order kinetic, whereas NH is left on the surface. Thus, with reactions (2b) and (7c), there exist two channels to produce ammonia and imine radicals. If one takes the measured desorption order of 1.34 to estimate the relative yield of the bimolecular and unimolecular reaction pathways, the latter accounts for about threequarter of the ammonia flux. The unimolecular pathway (2b) thus seems to be favoured over the bimolecular reaction (2c/7c). This requires that the energetic differences of the initial hydrazine decomposition into channel (2b) or (2c) are less significant. The given difference is largely determined by the binding energy of NH, where we used a value of 80 to 85 kcal/mol estimated in analogy to the binding energies of NH, compounds on Fe(111) [1]. If we lower the NH binding energy to 66 kcal/mol, measured for a Pt substrate [13], the bimolecular radical reaction (2c or 7c) would be favoured by about 17 kcal/mol over reaction (2b). This would yield a higher desorption order than experimentally determined. Thus, from the experimental desorption order it can be concluded that the NH binding energy onto Pd is about 80 to 85 kcal/mol or even higher. Both reactions (2b) and (7) leave NH bound to the surface or the equivalent of about 0.05 ML nitrogen. Unfortunately, we were not able to verify this conclusion by observing the corresponding nitrogen signal in our retarding field Auger electron spectrometer. From the intensities in TDS it can be concluded that this dissociative channel is several times (5–10) more likely than the desorption of intact N_2H_4 .

The low pre-exponential factors for both NH₃ and N_2H_4 desorption are interesting observations. This low desorption frequency can be understood when a molecular rearrangement from the adsorbed phase to the gas phase is necessary. A drastic conformational change of NH₃ from the gas phase to the adsorbed phase can hardly be imagined, because as an adsorbate ammonia should be bound to the metal via the N atom. Low pre-exponential factors are commonly observed when a reaction has to occur before the desorption. In this experiment ammonia is formed either by the bimolecular reaction (7) between two NH₂ radicals or by the decomposition of hydrazine (2b). Thus, in either case a reaction is involved. It also suggests that the decomposition of hydrazine (2b) does not occur upon dosing, but instead is initiated while heating the surface in TDS. For hydrazine, which desorbs in a first-order kinetic and which is the minority in the desorption flux, such a conformational change can be imagined. Also desorption from a specific site, e.g., steps, may be a possible explanation for the low pre-exponential factor in this case. The results obtained so far reveal an interesting and complex behaviour of the hydrazine interaction with Pd(100) and possibly other transition metals, which should warrant further investigations of this system.

Acknowledgement

We would like to thank Professor Comsa for making the crystal available to us, and the Deutsche Forschungsgemeinschaft for financial support (SFB 216, Teilprojekt P11). The comments of one of the referees were very helpful for improving the interpretation of the data.

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Pt [13], the bond energy of N atoms to Pd [11], and that of NH_3 and N_2H_4 on Pd measured in this work. We thus estimated binding energies of 80 to 85 and 55 kcal/mol for NH-Pd and NH_2 -Pd, respectively.

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