

Adsorption of Hydrazine on Iron Studied by X-Ray Photoelectron Spectroscopy†

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No studies on the interaction of hydrazine with iron surfaces have been reported although kinetic data for both molybdenum and tungsten systems¹ and an electron spectroscopic study of adsorption on copper have been published.² Whereas in the case of copper both core and valence-level spectroscopies indicated that adsorption was mainly associative in the temperature range 85 to 295 K, kinetic studies with tungsten suggested that dissociation of hydrazine occurred above 220 K. We are particularly concerned here with delineating the molecular events occurring by studying the individual species formed in possible dissociative processes at temperatures (85–295 K) where their inherent chemical reactivities are quenched. Recent studies^{3,4} of the interaction of N₂, NO, and NH₃ with iron, the assignment of various N(1s) peaks to particular surface species, and the general question of nitrogen fixation are further reasons for this investigation.

A Vacuum Generators (ESCA-3) electron spectrometer was used,⁵ iron surfaces were prepared by evaporation *in situ* in the spectrometer, and hydrazine was obtained from the Matheson Co. in 'lecture cylinders' and purified by vacuum distillation before use. The iron surfaces were free of contaminants as indicated by the absence of, for example, significant oxygen and carbon peaks in the O(1s) and C(1s) spectral regions. Further experimental details have been published elsewhere.^{2–5}

When an iron surface was exposed to hydrazine (600 L*) at 295 K [Figure 1(a)] an N(1s) peak developed at 397.3 eV with a FWHM value of about 2.5 eV. On evacuation and during cooling at a hydrazine pressure of 10⁻⁷ Pa to 85 K, two new N(1s) peaks emerged at about 398.5 and 400.5 eV. Exposure to hydrazine at 85 K enhanced the intensity of only the 400.5 eV peak. On warming the adlayer to 295 K *in vacuo* the 400.5 eV feature disappeared, the photoelectron spectrum [Figure 1(d)] being virtually identical with that observed initially at 295 K [Figure 1(a)]. The rather broad N(1s) peak at 295 K is a composite one, and since there is conclusive evidence^{3,4} for N(a) to be characterised by a value of about 397 eV we assign the lower binding energy component to this species. The 400.5 eV peak is due to weakly adsorbed molecular hydrazine. We now examine in more detail the 397–399 eV spectral region.

Figure 2 shows N(1s) spectra arising from the interaction of hydrazine with an iron surface at 295 K. We note that after an exposure of 60 L the peak is centred at 397.8 eV. However, at higher exposures (600 L) it moves to lower binding energy by about 0.6 eV. An analogous effect can be induced by thermal activation, the N(1s) value after heating the adlayer formed at 295 to 420 K being 396.8 eV.

† This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)*, 1977, issue no. 2, p. iv]; there is therefore no corresponding version in *J. Chem. Research (M)*.

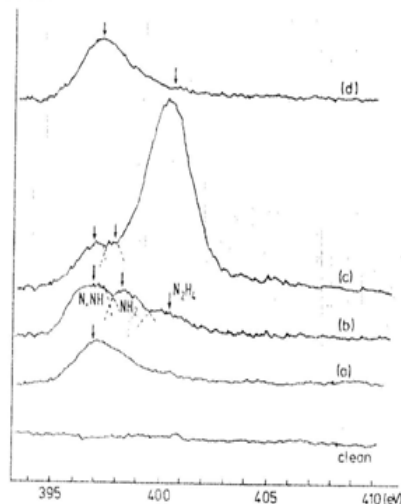


Figure 1 N(1s) spectral region for clean iron surface; after adsorption of hydrazine at 295 K [curve (a)], evacuation and subsequent cooling to 85 K in hydrazine at about 10⁻⁷ Pa [curve (b)]; after further exposure to hydrazine at 85 K [curve (c)] and warming to 295 K *in vacuo* [curve (d)]. Arrows indicate the main N(1s) peaks. In all the experiments the hydrazine pressure was about 10⁻⁴ Pa. Analysing conditions: f.s.d: 10⁴ counts s⁻¹, 100 eV analysing energy.

Note: Instrumental sensitivity is substantially smaller in these experiments than for the data reported in Figures 2 and 3.

We suggest that a reaction between NH(a) and N₂H₂(g) occurs (eqn. 1) at high exposure leading to a drift in the peak position to lower binding energy.



Therefore at 295 K (Figure 1) the species responsible for the broad N(1s) peak (396–399 eV) are suggested to be N(a) and partially hydrogenated (NH, NH₂) species. We have no means of distinguishing unambiguously between NH(a) and NH₂(a), although in earlier work² we assigned, on the basis of the stoichiometry of the process, an N(1s) value of 398 eV to NH(a). Since there is evidence⁶ from both experimental studies and molecular orbital calculations for a roughly linear relationship between the negative charge on the nitrogen atom and the N(1s) value, we suggest the following assignments: N, 397 eV; NH, 398 eV; NH₂, 399 eV.

Consider next the thermal activation of an adlayer formed on a clean iron surface at 85 K. After an exposure to hydrazine (90 L) a single N(1s) peak centred at 400.5 eV was observed. This is due to molecularly adsorbed hydrazine. On warming, the intensity of this peak diminished until at 233 K it was about a sixth of that at 85 K (Figure 3); the binding energy had not changed, but some tailing to lower binding energy was visible. By comparing the

*1 Langmuir = 10⁻⁶ Torr s.

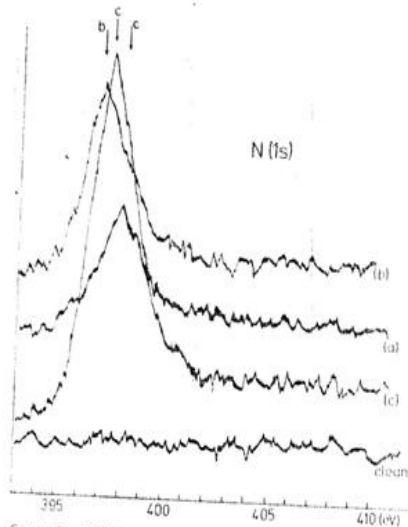


Figure 2 N(1s) spectral region for: clean Fe surface, after exposure (60 L) of Fe surface to $N_2H_4(g)$ at 295 K [curve (a)] and then heating to 420 K [curve (b)]; after exposure (600 L) of Fe surface to $N_2H_4(g)$ at 295 K [curve (c)]
Analyzing conditions: f.s.d.: 3×10^3 counts s^{-1} , 100 eV

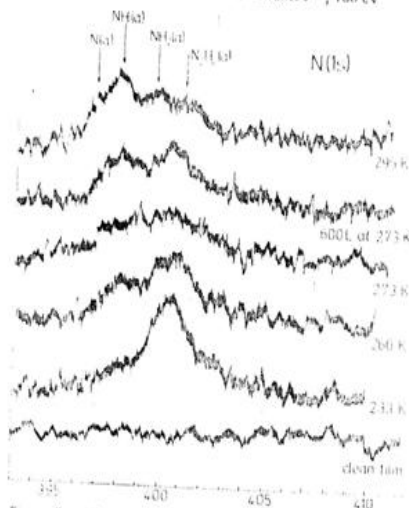


Figure 3 N(1s) spectra observed during warming of the hydrazine adlayer formed at 85 to 273 K. Between 85 and 233 K no new N(1s) features developed but the intensity of the 400.5 eV peak decreased substantially. The surface at 273 K was further exposed (600 L) to $N_2H_4(g)$ and warmed finally to 295 K.
Analyzing conditions: f.s.d.: 3×10^3 counts s^{-1} , 100 eV

intensities of the N(1s) and the no-loss Fe(2p_{3/2}) peaks using the procedure described elsewhere² we estimate that, from the N(1s): Fe(2p_{3/2}) area ratio (0.0104), at 233 K the concentration of 'nitrogen' species present is $0.4 \times 10^{15} \text{ cm}^{-2}$ or 0.2×10^{15} hydrazine molecules per cm^2 . If the adsorbed hydrazine molecule occupies about 20 \AA^2 the coverage is approximately half a monolayer. At 260 K a new peak emerged at about 398 eV, while at 273 K there was present a broad peak of low intensity with

possible maxima at about 397.5 and 400.5 eV (Figure 3). These maxima became more obvious on further exposure to hydrazine (600 L) at 273 K. Warming the adlayer to 295 K transferred some of this intensity to the 397 eV region of the spectrum.

A significant point to note, and crucial to the mechanism of the interaction at low temperature, is that the surface after warming to room temperature (Figure 3) is apparently unreactive to $N_2H_4(g)$ even though the total N(1s) intensity is only about 10% of that observed with a clean surface at the same temperature (Figure 2). Clearly the active surface sites are poisoned by hydrogen adatoms still present at 295 K and not observable by X-ray photoelectron spectroscopy. There is obviously a regeneration mechanism occurring during the interaction with a 'clean' surface at 295 K (Figures 1 and 2) and presumably involving desorption of N_2 , NH_3 , and H_2 . These are the usual gaseous products in the decomposition of N_2H_4 by metals.

We suggest that between 85 and 233 K the predominant process is N-H bond cleavage of the molecularly adsorbed N_2H_4 . This is followed by nitrogen desorption [the N(1s) signal was observed other than from molecularly adsorbed N_2H_4 , Figure 3] and hydrogen chemisorption, now well known³ to be inactive in both associative and dissociative chemisorption of H₂. There is, however, some evidence for N-N cleavage at 233 K in that N(1s) intensity is discernible in the 397-399 eV region (Figure 3). Above 233 K, N-N cleavage occurs more readily with the formation of NH and NH₂ species, but this process occurs to only a limited extent (Figure 3) because of the active sites being blocked by H₂. Further exposure to $N_2H_4(g)$ at 273 K results in the conversion of NH₂ into NH₃ (eqn. 1) with the consequent development of intensity at about 397 eV.

The present study provides direct spectroscopic evidence for the participation of dehydrogenated (NH and NH₂) surface species, and nitrogen and hydrogen adatoms, as well as the unreactively adsorbed molecule in the catalytic decomposition of hydrazine by iron. A quantitative model of the decomposition should emerge from studies of model crystal surfaces, and from combining electron spectroscopic studies of the surface species with mass spectrometric analysis of the gas phase.

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