JOURNAL OF CATALYSIS 6, 20–25 (1966)

The Adsorption of Hydrogen Cyanide on Evaporated Films of Nickel and Tungsten

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Received July 12, 1965

Using an ultra-high-vacuum system, the adsorption of hydrogen cyanide has been studied on evaporated films of nickel and tungsten at 0°C. Adsorption was studied on surfaces that were initially bare and also on surfaces upon which hydrogen or deuterium had been preadsorbed.

At low values of θ_{CN}, adsorption required two surface sites and occurred by both dissociative and nondissociative mechanisms. As the coverage increased, both of these adsorption modes were of diminished importance relative to a one-site nondissociative species. The structure of these surface species is considered and their relevance to catalytic exchange and hydrogenation of hydrogen cyanide is discussed.

INTRODUCTION

Anderson and Clark (*1*) recently studied the reaction of hydrogen cyanide and hydrogen over evaporated metal films. The way in which the hydrogen cyanide molecule is adsorbed on the metal surface is clearly relevant to this, and it was for this reason that the present study was undertaken. Except for a few measurements made by Anderson and Clark (*1*), we know of no previous work on the adsorption of hydrogen cyanide on clean metal surfaces.

EXPERIMENTAL

Standard ultra-high-vacuum techniques were used. Pressures less than about 5×10^{-4} torr in the system were measured with an ionization gauge (Speedivac IG3H). During film deposition, the reaction volume was isolated from the gas dosing system and from the mass spectrometer by means of breakable glass seals. Pressures greater than about 5×10^{-4} torr in the system were measured with a thermistor gauge (Stantel U23) calibrated for hydrogen and for hydrogen cyanide. Gas doses were prepared in a McLeod gauge in the dosing system, and gas was admitted via a refrigerated trap. Hydrogen, deuterium, and hydrogen cyanide were prepared and handled as previously described (*1*). The dosing system was of conventional high-vacuum design and could be evacuated to 10^{-6}–10^{-7} torr. The last valve between the dosing system and the adsorption apparatus was an all-metal Hoke valve.

The seal to the mass spectrometer leak was broken at different times during various experiments and, once broken, corrections for leakage were made to the amount of gas in the reaction volume. Some control over the leak rate was available since the leak consisted of a 10-cm length of 1-mm diameter ground tungsten rod which could be moved in and out of a length of 1-mm bore precision glass capillary. The leak could be isolated from the system by an all-glass ball-and-socket valve; both were operated magnetically.

After baking, the residual pressure in the system was about 10^{-9} torr. Metal films were deposited in the manner previously described (*2*). During tungsten evaporation, the pressure remained at about 10^{-9} torr. However.

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during nickel evaporation the pressure was about 10^{-8} torr.

The mass spectrometer was an MS10. It was operated at about 30 eV for the analysis of hydrogen and deuterium, and at about 17.5 eV for hydrogen cyanide and other products. Corrections for fragmentation and for natural isotopic abundances were made where necessary. The tubulation between the adjustable leak and the mass spectrometer could also be outgassed by baking.

Unless otherwise specified, all experiments were carried out with the metal film at 0°C.

Results

Film areas were estimated either from hydrogen adsorption data (before the admission of hydrogen cyanide), or by the BET method using xenon at 90°K at the completion of an experiment; in either case the same method and the same assumptions concerning the number of metal atoms per unit area of surface were used as described previously (*2*). Where both methods were used, the areas agreed to within about 10%. In the following discussion, θ_X (e.g., θ_H, θ_{CN}) is defined so that $\theta_X = 1$ corresponds to a *stoichiometry* of one X group for each surface metal atom. It should be noted that the symbols θ_{CN} and θ_H are used without detailed implications as to the nature of the adsorbed species or the mode of adsorption. In particular, θ_{CN} refers to a surface species in which the carbon and nitrogen atoms remain bonded together, but without implication as to the presence or absence of an attached hydrogen atom.

Adsorption of hydrogen cyanide on baked glass was much diminished compared with adsorption on unbaked glass reported previously (*1*). In reporting hydrogen cyanide uptakes on metal films, the results have been corrected for glass adsorption, but this correction was always less than 10% of the total.

Adsorption of hydrogen cyanide at 0°C onto virgin metal films resulted in immediate and irreversible adsorption up to about $\theta_{CN} \simeq 0.5$, and in the range $0 < \theta_{CN} \lesssim 0.5$ the equilibrium hydrogen cyanide pressure was $<10^{-5}$ torr and no hydrogen (or any other substance) was returned to the gas phase. In the case of nickel, the addition of further doses of hydrogen cyanide to the system resulted in slow adsorption to give $\theta_{CN} > 0.5$ with the hydrogen cyanide pressure over the film now in the range 10^{-3}–10^{-2} torr. Under these latter conditions adsorption equilibrium could not be achieved, since very slow processes extending into some hours' duration were observed and which resulted in increased values of θ_{CN}, with corresponding falls in hydrogen cyanide pressure. Values of θ_{CN} up to about 0.9 were observed in this way. During adsorption in the range $\theta_{CN} > 0.5$, some hydrogen was desorbed to the gas phase, but this amounted to no more than about 5% of the total hydrogen adsorbed.

In a number of experiments, hydrogen (or deuterium) was adsorbed at 0°C on the film to an equilibrium pressure of about 10^{-2} torr prior to the adsorption of hydrogen cyanide. The excess hydrogen was then pumped away from the gas phase and the hydrogen cyanide adsorbed onto a "hydrogen-covered" surface. For hydrogen-covered surfaces prepared in this way θ_H was not accurately defined since the pumping procedure undoubtedly removed some hydrogen from the surface. However, from the hydrogen adsorption isotherms (*2*) and heats of adsorption (*3*, *4*), this loss is estimated at not more than about 10% when pumped to 10^{-6} torr. A correction of this magnitude has been applied where necessary.

Detailed isotherms were not measured for the adsorption of hydrogen cyanide onto hydrogen-covered surfaces. However on both metals, coverages of $\theta_{CN} <$ about 0.4 were achieved at equilibrium hydrogen cyanide pressures $< 10^{-5}$ torr. On nickel θ_{CN} reached the range 0.8–0.9 at $p_{HCN} \simeq 2 \times 10^{-2}$ torr, while on tungsten θ_{CN} reached about 0.5 at the same pressure. No slow processes were observed on hydrogen-covered surfaces. During the adsorption of hydrogen cyanide on hydrogen-covered films, hydrogen was desorbed from the surface. Figure 1(a) shows the way in which the total amount of desorbed hydrogen increased as the coverage by adsorbed cyanide increased. The amount of desorbed hydrogen is expressed relative to the total number of surface adsorption

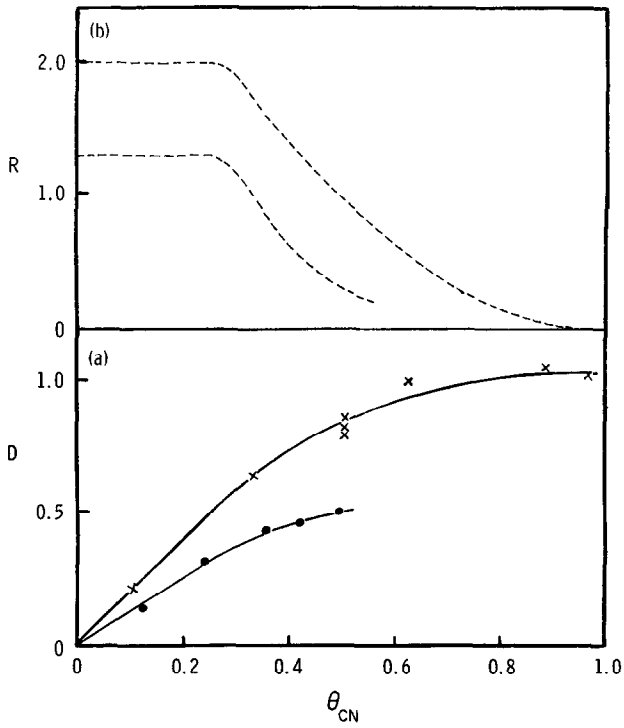


FIG. 1. (a) Variation of D with θ_{CN}, where D is the ratio of the number of hydrogen atoms desorbed (as H_2) to the total number of surface sites on the film; ×, nickel; ●, tungsten. (b) Variation of R with θ_{CN}, where R is the number of hydrogen atoms desorbed (as H_2) per adsorbing HCN molecule; upper curve, nickel; lower curve, tungsten.

sites, so that experiments with films of different areas can be scaled together. The slope of the line at any point equals the number of hydrogen atoms desorbed per adsorbed hydrogen cyanide molecule (R) and the resulting values of R are plotted against θ_{CN} in Fig. 1(b). No desorption products other than hydrogen were detected in the mass spectrometer, even on heating to 180°C. However, some separate experiments with methylamine showed that adsorption of this substance at room temperature on baked glass was severe. Thus, small amounts of amines could have been desorbed in the hydrogen cyanide experiments and yet remained undetected because of their being scavenged onto the glass before reaching the mass spectrometer. Nevertheless, it is clear that if methylamine had been formed, it could only have been in relatively small amounts.

The degree of reversibility of hydrogen cyanide adsorption on nickel at 0°C was checked in the following way: On a virgin nickel film was adsorbed $HC^{13}N$ (57.5 atom % C^{13}) to the extent of 10.5×10^{17} molecules, corresponding to $\theta_{CN} = 0.81$ and with $p_{HCN} = 1.73 \times 10^{-2}$ torr. The gas phase was then pumped away and a dose of 9.01×10^{17} HCN molecules added; of this 0.48×10^{17} molecules were adsorbed and p_{HCN} was then 2.2×10^{-2} torr. Mass spectrometric examination of the 26/27 and 27/28 peak-height ratios showed that no $HC^{13}N$ had been returned to the gas phase during the adsorption of HCN. A similar negative result indicating irreversible adsorption was obtained with hydrogen cyanide adsorbed to an equilibrium pressure of 2.5×10^{-3} torr on a hydrogen-covered nickel surface.

The hydrogen present on the surface as a result of the adsorption of hydrogen cyanide

on bare nickel was shown to be inert to exchange with gas-phase deuterium. Hydrogen cyanide was adsorbed at 0°C on virgin nickel to give $\theta_{CN} = 0.85 \simeq \theta_H$ at $p_{HCN} = 2.2 \times 10^{-2}$ torr. After pumping away the gas phase, a dose of 8.0×10^{17} D_2 molecules was added. None was adsorbed and no HD (or H_2) was detected in the gas phase after standing for 30 min at 0°C. The addition of 5.0×10^{17} H_2 molecules resulted in no production of HD even on heating to 77°C for 30 min.

It was found that adsorption of hydrogen cyanide onto a deuterium-covered surface resulted in some exchange during the *act* of adsorption. In one such experiment, hydrogen cyanide was adsorbed onto a deuterium-covered nickel surface to the extent of 7.85×10^{17} molecules corresponding to $\theta_{CN} = 0.50$; the desorbed "hydrogen" contained 4.65×10^{17} H atoms or 59% of the amount of hydrogen in the HCN adsorbed. In a similar experiment, hydrogen cyanide was adsorbed onto a deuterium-covered nickel surface to the extent of 8.73×10^{17} molecules corresponding to $\theta_{CN} = 0.61$; the desorbed "hydrogen" contained 6.04×10^{17} H atoms or 69% of the amount of hydrogen in the HCN adsorbed. The gas phase was then pumped away and a dose of 6.10×10^{17} D_2 molecules was added, with $p_{D_2} = 1.54 \times 10^{-2}$ torr. Mass spectrometric examination of the gas phase 5 min later showed that the HD/D_2 ratio was 1/12.8, no H_2 could be detected, and the gas-phase composition did not change with time. The pressure remained unchanged and these data correspond to the presence of 4.8×10^{16} hydrogen atoms in the gas phase (as HD). For comparison, if exchange equilibrium had been reached, the gas phase would have contained 1.1×10^{16} H_2 molecules and 1.4×10^{17} HD molecules, or a total of 1.6×10^{17} H atoms, which is greater than the value observed by a factor of 3.3. No DCN was detected.

Discussion

Lack of exchange, using C^{13} labeling, between adsorbed and gas-phase hydrogen cyanide indicates that the adsorbed material was strongly bonded to the surface. For this reason we will not discuss further a species π-bonded to the surfaces.*

It was found that the hydrogen on the surface as a result of adsorption of hydrogen cyanide to $\theta_{CN} = 0.85$ on initially bare nickel could not be exchanged with gas-phase deuterium. Since hydrogen chemisorbed as H*† on a nickel film is known to exchange rapidly with deuterium at 0°C (5), we conclude that none of the hydrogen on the surface could have been present as H*, and therefore the hydrogen cyanide was adsorbed nondissociatively. The corresponding result relating to adsorption on a deuterium-covered surface is somewhat more complex. In this case, the "hydrogen" returned to the gas phase contained a portion of the hydrogen from the adsorbed hydrogen cyanide. For instance, in adsorption to give $\theta_{CN} = 0.61$, 69% of the hydrogen was desorbed in this way and 31% remained on the surface. However, of this hydrogen remaining on the surface, only a small proportion (18%) could be subsequently exchanged with a large excess of gas-phase deuterium and we identify this with the small amount of H* that must have been present. The bulk of the hydrogen on the surface that was not exchangeable we consider to be present in a form similar to that resulting from adsorption on an initially bare surface. The exchange that occurred with D* in the act of HCN adsorption is *prima facae* evidence that part of the adsorption occurred by a dissociative mechanism such as (2) below.

The results in Fig. 1 show that at $\theta_{CN} <$ about 0.25, adsorption of hydrogen cyanide onto hydrogen-covered nickel gave a value of $R = 2$. This is consistent with processes (1) and (2)

$$2H_* + HCN \rightarrow (H_*CN_*) + H_2 \quad (1)$$

$$H_* + HCN \rightarrow {}_*CN + H_2 \quad (2)$$

where (H*CN*) represents a nondissociatively adsorbed hydrogen cyanide bound to

* However, at higher hydrogen cyanide pressures, a relatively weakly adsorbed π-bonded species may possibly occur on the surface.

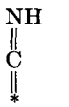
† Throughout this discussion, an asterisk * is used to represent an adsorption site.

two surface sites. In terms of conventional valence requirements, two structures for (H*CN*) must be considered

(A) (B)

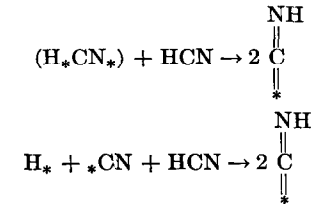
The likelihood of (A) must be considered in the light of the observation that an =N–H absorption in the infrared results from hydrogen cyanide adsorbed on metal oxides (*6*), while (B) is a likely precursor to hydrogen cyanide hydrogenation (*1*). The observed rapid adsorption up to $\theta_{CN} \simeq 0.5$ on initially bare nickel is consistent with process (1) as well as with dissociative adsorption to give *CN and H*.

It is clear that at $\theta_{CN} >$ about 0.25, adsorption cannot be described by reactions (1) and (2) only; R is less than two and approaches zero as $\theta_{CN} \rightarrow 1$. The total number of hydrogen atoms desorbed in reaching $\theta_{CN} \simeq 1$ on nickel approximately equals the number initially adsorbed in producing the hydrogen-covered surface. Furthermore, little hydrogen was evolved on reaching $\theta_{CN} \simeq 1$ on initially bare nickel. Therefore, the average surface composition at $\theta_{CN} \simeq 1$ on nickel is one hydrogen atom per cyanide residue and each residue occupies one surface metal atom or site. The most reasonable structure for this residue is



(C)

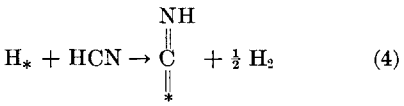
Since the formation of (C) at high coverages requires $R > 0$, we write



(3a)

(3b)

The formation of species (C) will clearly be favored as the coverage increases and the chance becomes smaller of finding a pair of adjacent sites unoccupied by cyanide. However, when only a single site is available on a hydrogen-covered surface, (C) may be formed by



(4)

for which $R = 1$. Here we assume that surface diffusion makes possible the recombination of hydrogen atoms to give molecular hydrogen.

We thus propose that hydrogen cyanide adsorption on nickel proceeds at low coverages by a two-site mechanism and thus $R = 2$ on a hydrogen-covered surface. There is evidence that on a hydrogen-covered surface, both dissociative [reaction (2)] and nondissociative adsorption [reaction (1)] occurred. This may also be the case on an initially bare surface, but if so it is clear that as the coverage is increased, reaction (3b) must occur, since on reaching $\theta_{CN} =$ 0.85 no exchangeable hydrogen was present and <5% had been desorbed. As the coverage increases some single sites are isolated on the surface and on these, adsorption may occur to give (C) with $R = 1$ on a hydrogen-covered surface. Furthermore, adsorption of hydrogen cyanide can also proceed by reactions (3) for which $R = 0$, and this becomes more important as the number of sites diminishes.

The species (A) and (C) are very similar to the two forms in which carbon monoxide has been shown by infrared evidence (*7*) to be present on platinum, while there is evidence from adsorption measurements (*8*) for one or other of these forms of carbon monoxide on a variety of metals.

It is also seen from Fig. 1 that on tungsten R is less than two over the whole coverage range studied. In particular $R \simeq 1.3$ out to $\theta_{CN} \simeq 0.25$, suggesting that two-site species and one-site species are produced with comparable *a priori* facility; if formed with exactly equal chance a value of $R = 1.5$ would have resulted. The fall in R with

increasing coverage then occurs in a way similar to that on nickel.

Species (B) is analogous to that suggested (*9*) as required for the hydrogenation of acetylene. Thus, the fact that no or only a very little methylamine was formed from the adsorption of hydrogen cyanide on hydrogen-covered nickel suggests that there was little of species (B) relative to (A). Furthermore, it is easier, on steric grounds, to understand the considerable inertness to exchange of the hydrogen in (A) than in (B). The relative efficiencies of different metals for hydrogen cyanide hydrogenation (*1*) may depend upon the proportion adsorbed as (B). The conclusion that at high coverage very little adsorbed hydrogen cyanide is present in a dissociative form correlates with the very low frequency factor found (*1*) for HCN/D_2 exchange.

Acknowledgments

One of us (N.J.C.) is grateful for the award of a Commonwealth Postgraduate Scholarship. We wish to acknowledge a grant made to one of us (J.R.A.) by the executive of CSIRO for the purchase of the MSIO, and to acknowledge a grant by Imperial Chemical Industries (ANZ) for the purchase of vacuum equipment.

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