

Intermolecular Hydrogen Transfer in Nitrile Hydrogenation over Transition Metal Catalysts

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In the co-hydrogenation of deuterio-acetonitrile (CD_3CN) and butyronitrile ($\text{C}_3\text{H}_7\text{CN}$) over SiO_2 -supported Pt and Ru catalysts, H atoms are preferentially added to the C atom of the CN groups, but D atoms are added to the N atom. This shows that intermolecular hydrogen transfer from acetonitrile to the nitrogen atom of CN groups takes place. The methyl group of acetonitrile is a more effective donor of hydrons than the propyl group in butyronitrile. Hydrogen transfer is most efficient for breaking the strong $\text{N}=\text{M}$ chemisorption bond, releasing an amine molecule to the gas phase. The *cis*-insertion of an alkyl group into an $\text{N}=\text{M}$ bond leads to a secondary amine. © 2000 Academic Press

Key Words: nitrile hydrogenation; transition metals; isotopic labeling; hydrogen transfer; reaction mechanism.

I. INTRODUCTION

When converting nitriles into deuterio-amines over transition metal catalysts in a large excess of D_2 , we were surprised to find that significant amounts of the product molecules contain fewer D atoms than predicted by the straightforward stoichiometry for nitrile hydrogenation. Even more surprisingly, it appeared that D atoms are preferentially added to the C atom of the CN group, but H atoms are added to the N atom (1). For instance, the predominant isotopomers of diethylamine obtained by reacting acetonitrile with D_2 are $(\text{CH}_3\text{CD}_2)_2\text{NH}$, $(\text{CH}_3\text{CD}_2)\text{-NH-}(\text{CD}_2\text{CD}_3)$, and $(\text{CD}_3\text{CD}_2)_2\text{NH}$. As no H_2 was present in the feed, the only conceivable source for the H atoms in the amine group was the methyl groups of acetonitrile.

Two hypothetical routes have been considered for the deviation from overall stoichiometry and the specific direction of some H atoms to become attached to the N atom of an adsorbed nitrile:

(1) Initially, an overlayer of polymerized nitrile is formed on the catalyst. The further reaction is a two-step process:

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H atoms from the overlayer are transferred to adsorbed nitrile molecules; the resulting holes in the overlayer are subsequently filled by interaction with D_2 . Clearly, this process would explain deviations from simple reaction stoichiometry for short reaction times. At longer times, however, the mobile hydrogen in the overlayer should be replaced by deuterium and the product composition should be either that of the simple stoichiometry or one richer in D, if secondary H/D exchange occurs. Indications for this two-step process have indeed been found, but it was also observed that even after extended reaction time the hydrogen atoms in the amine were still preferentially of the light isotope. To explain this, the second hypothesis is of interest.

(2) Hydrons are transferred from the CH_3 -group of some CH_3CN molecules to the N atom of adsorbed amine precursors. This model requires C–H bond rupture of CH_3CN molecules and is in line with our previous results that significant H/D exchange of acetonitrile takes place under the condition of nitrile hydrogenation or deuteration. To examine this possibility the co-hydrogenation of butyronitrile and D-labeled acetonitrile has been carried out in the present study over SiO_2 -supported Pt and Ru catalysts. The reaction product was analyzed by a combination of GC and mass spectrometry as described in our previous paper (1).

II. EXPERIMENTAL

Pt/ SiO_2 was prepared by impregnation of silica with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$; the Pt loading was about 1%. Ru/ SiO_2 was prepared by impregnation of silica with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$; the Ru loading was about 3%.

Prior to reduction, Pt/ SiO_2 was calcined in a flow of O_2 of 100 mL/min at 400°C for 2 h with a ramping rate of $0.5^\circ\text{C}/\text{min}$, but the Ru/ SiO_2 catalyst was heated in an Ar flow of 60 mL/min at 450°C for 20 min. *In situ* reduction was carried out in an H_2 flow of 40 mL/min at 400°C for 30 min. The reactions were carried out in a micro-flow fixed-bed reactor. One-hundred-milligram catalysts were used. The reaction temperature was 100°C over Pt/ SiO_2 and 125°C over Ru/ SiO_2 . The feed stream was obtained by passing two

H₂ flows of 20 mL/min through two saturators filled with acetonitrile (−4°C) and butyronitrile (25°C), respectively, and mixing the flows. The partial pressure of each nitrile in the stream was about 10 Torr. In calculating nominal conversions, it was assumed that the partial pressure of the nitriles was equal to the equilibrium pressures in the saturator. However, apparent deviations from the material balance can arise when yields of the mixed products butyl-ethylamine, butyl-diethylamine, and dibutyl-ethylamine are calculated from the measured selectivities and the nominal conversions of acetonitrile and butyronitrile. If under flow conditions the actual partial pressure is lower, this will lead to a systematic overestimation of the conversions. No attempt was made to correct for this error, as the present research is focused on D/H distribution in the reaction products, and saturator temperatures and flow rates were always kept constant when different catalysts were compared.

An HP-5890 GC equipped with an HP-1 capillary column (5 m × 0.53 mm) was used for on-line analysis of hydrogenation. A GC-MS (HP-G1800A GCD system) equipped with an HP-PONA column (50 m × 0.2 mm) was used for mass spectral analysis off-line. The reaction products were trapped by liquid nitrogen and, after warming up to 0°C, were analyzed by GC-MS. Then, the products were subjected to a secondary exchange with liquid D₂O by shaking well. These products were again analyzed by GC-MS.

III. RESULTS

1. Co-hydrogenation of D-Labeled Acetonitrile and Butyronitrile over Pt/SiO₂

Co-hydrogenation of acetonitrile (CD₃CN) and butyronitrile (*n*-C₃H₇CN) was carried out over Pt/SiO₂ at 100°C. The reaction products include; diethylamine (DEA), triethylamine (TEA), and ethane; butylamine (BA), diethylamine (DBA), tributylamine (TBA), and butane; butylethylamine (BEA), butyl-diethylamine (BDEA), and dibutyl-ethylamine (DBEA). At 30 min TOS, the nominal conversion of acetonitrile is 22.6%; the selectivities (in mol%) of acetonitrile conversion are 10.1 to DEA, 7.9 to TEA, 6.0 to BEA, 35.6 to BDEA, and 30.9 to DBEA; the nominal conversion of butyronitrile is 62.9%, and the selectivities (mol%) of butyronitrile are 0.4 to BA, 4.6 to BEA, 13.7 to BDEA, 2.9 to DBA, 47.4 to DBEA, and 25.6 to TBA.

The "initial" products after 30 min reaction time were collected in a liquid nitrogen trap and analyzed by GC-MS. They were subsequently subjected to secondary exchange with D₂O and analyzed again by GC-MS. As shown before, reaction with D₂O exclusively exchanges those hydrogens that are bonded to the N atoms (2–4); this procedure permits us to identify which D atoms in an amine are bonded to N and which are bonded to C atoms. The MS spectra show

that extensive H/D exchange of acetonitrile (CD₃CN) takes place. Only a few mass spectra are presented in the present paper. The other mass spectra are available upon request.

Figure 1 shows the mass spectra of ethylamine in the fresh products and after secondary exchange with D₂O. The main fragmentation of ethylamine in the MS is loss of one methyl group (5). In the fresh product, the highest molecular ion and the highest main fragmentation ion are observed at *m/e* = 50 and at *m/e* = 32, respectively. This indicates the presence of two D atoms in the amine fragmentation ion -CH₂NH₂, so the methyl group must be -CD₃. The relatively high abundance of the ion at *m/e* = 49 in comparison to *m/e* = 50 indicates the presence of methyl groups with less than three D atoms owing to H/D exchange at the catalyst surface. After the secondary exchange with D₂O, the molecular ion and main fragmentation ion are still at *m/e* = 50 and at *m/e* = 32. It follows that the ethylamine product of the co-hydrogenation over Pt/SiO₂ has the composition CD₃CH₂ND₂.

Figure 2 shows the mass spectra of diethylamine in the fresh product. After secondary exchange with D₂O, the spectrum is almost identical. The molecular ion and main fragmentation ion caused by the loss of a methyl group are observed at *m/e* = 80 and *m/e* = 62, respectively. The results show that most diethylamine molecules have the composition (CD₃CH₂)₂ND.

Mass spectral analysis has been applied to the other products. Butyl-ethylamine has the prevalent formula (CD₃CH₂)-ND-(CH₂CH₂CH₂CH₃); its molecular ion is at *m/e* = 105, and the fragmentation ions are at *m/e* = 87, due to the loss of a CD₃ group, and at *m/e* = 62, due to the loss of a propyl group.

The presence of two isotopomers in the dibutylamine product is detected by GC-MS. The isotope effect of the GC analysis leads to a shorter retention time for molecules with higher D content (6–8). MS analysis of the thus-separated products shows that one isotopomer has the composition (CH₃CH₂CH₂CH₂)₂ND, its molecular ion has *m/e* = 130, and the main fragmentation ion has *m/e* = 87 due to the loss of a propyl group. The other isotopomer is (CH₃CH₂CD₂CH₂)₂ND, with the molecular ion at *m/e* = 136 and the main fragmentation ion at *m/e* = 91. The relative abundance of the latter isotopomer is very low.

As tertiary amines have no N-bonded hydrogens, their mass spectrum does not change upon treatment with D₂O. Figure 3 shows the mass spectrum of triethylamine. The molecular ion is at *m/e* = 107; the main fragmentation ions are at *m/e* = 89, due to the loss of a CD₃ group, and at *m/e* = 92, due to the loss of a CH₃ group with high abundance. The abundance of the ion at *m/e* = 89 is approximately twice that at *m/e* = 92. The results demonstrate that the predominant molecule is (CD₃CH₂)₂-N-(CH₂CH₃).

For diethyl-butylamine, (CH₃CH₂CH₂CH₂)-N-(CH₂CH₃)(CH₂CD₃), the molecular ion is at *m/e* = 132. The

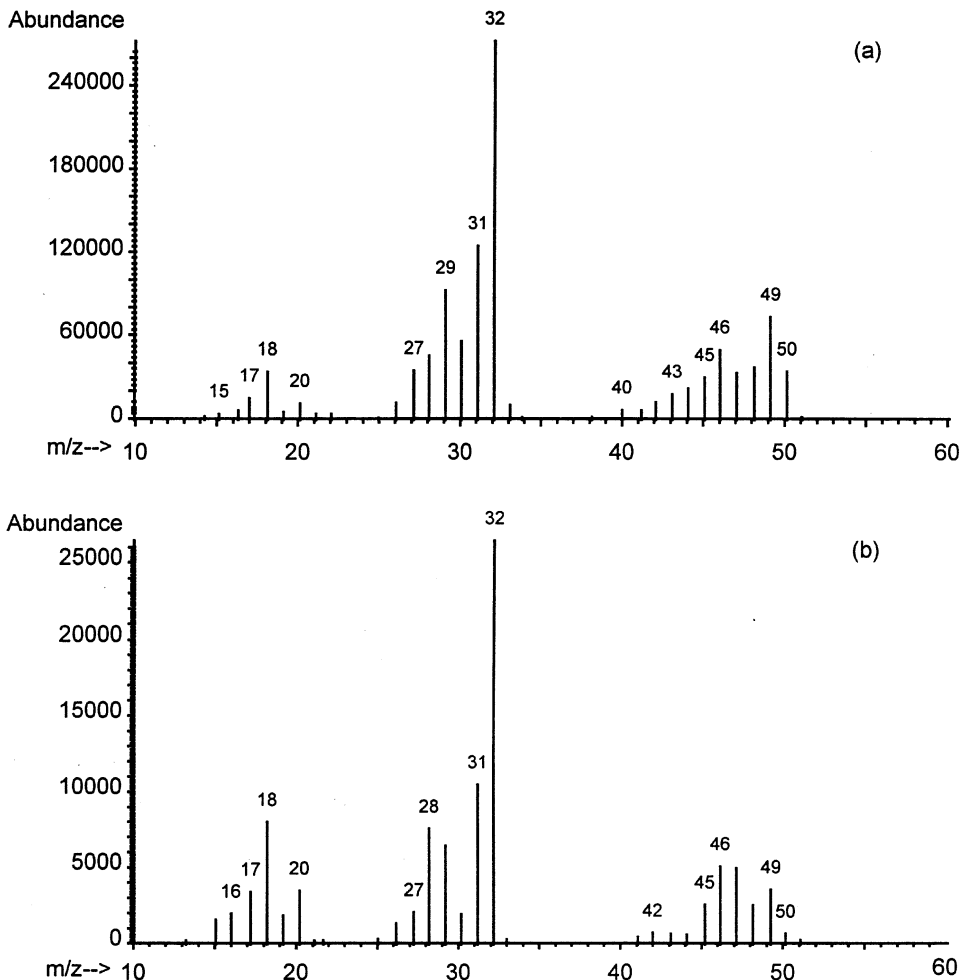


FIG. 1. Mass spectra of ethylamine formed in the hydrogenation of $\text{CD}_3\text{CN} + n\text{-C}_3\text{H}_7\text{CN}$ over Pt/SiO_2 at 100°C : (a) fresh products; (b) after secondary exchange with D_2O .

fragment at $m/e = 117$ is due to the loss of one CH_3 group, the peak at $m/e = 114$ is due to the loss of one $-\text{CD}_3$ group and at $m/e = 89$ due to the loss of one $\text{CH}_3\text{CH}_2\text{CH}_2-$ group.

Dibutyl-ethylamine has two isotopomers. One is $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{-N-(CH}_2\text{CH}_3)$. It has a molecular ion at $m/e = 157$ and fragmentation ions at $m/e = 142$, due to the loss of $-\text{CH}_3$ group, and at $m/e = 114$, due to the

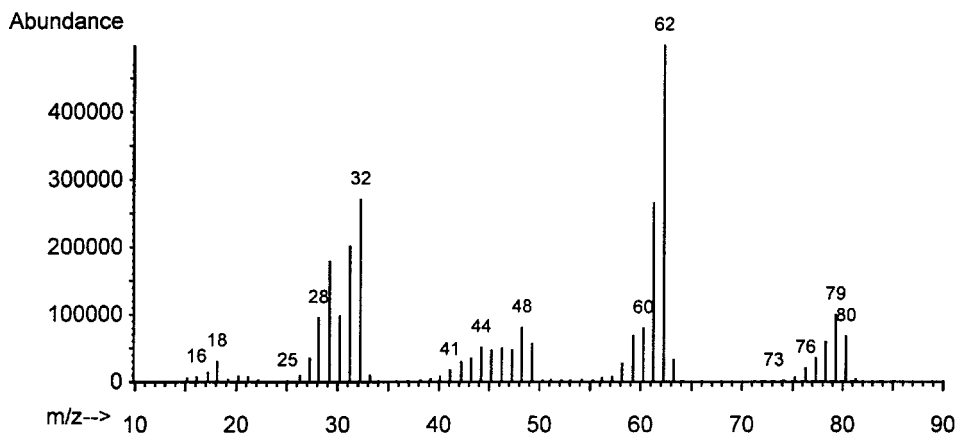


FIG. 2. Mass spectra of diethylamine formed in the hydrogenation of $\text{CD}_3\text{CN} + n\text{-C}_3\text{H}_7\text{CN}$ over Pt/SiO_2 at 100°C .

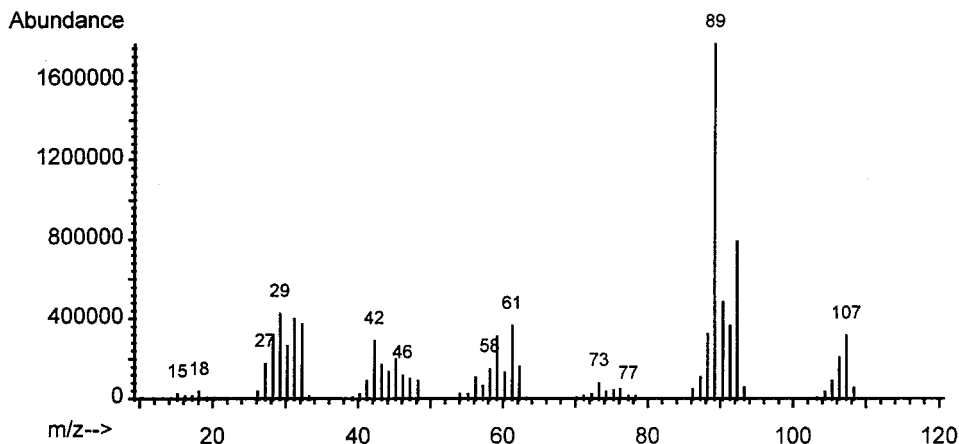


FIG. 3. Mass spectra of triethylamine formed in the hydrogenation of $\text{CD}_3\text{CN} + n\text{-C}_3\text{H}_7\text{CN}$ over Pt/SiO_2 at 100°C .

loss of a $\text{CH}_3\text{CH}_2\text{CH}_2\text{-}$ group. The other isotopomer is $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{-N-(CH}_2\text{CD}_3)$; it has molecular ion at $m/e = 160$ and fragmentation ions at $m/e = 142$, due to the loss of a -CD_3 group, and at $m/e = 117$, due to the loss of a $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ group. The relative abundance of the latter isotopomer is very low.

The tributylamine product has the composition $(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$. It has a molecular ion at $m/e = 185$ and a main fragmentation ion at $m/e = 142$ caused by loss of a propyl group.

2. Co-hydrogenation of D-Labeled Acetonitrile and Butyronitrile over Ru/SiO_2

Co-hydrogenation of D-labeled acetonitrile (CD_3CN) and butyronitrile was carried out over Ru/SiO_2 at 125°C . At 30 min TOS, the conversion of acetonitrile is 7.3%, and the selectivities (mol%) of the acetonitrile conversion are 43.2 to ethylamine, 17.9 to ethylidene-ethylamine, 18.3 to ethylidene-butylamine and butylidene-ethylamine, and 11.6 to butyl-ethylamine; the conversion of butyronitrile is 17.5%, and the selectivities (mol%) of butyronitrile conversion are 33.8 to butylamine, 15.4 to ethylidene-butylamine and butylidene-ethylamine, 9.8 to butyl-ethylamine, 23.6 to butylidene-butylamine, 16.0 to dibutylamine, and 1.5 to tributylamine. The present results do not distinguish between ethylidene-butylamine and butylidene-ethylamine.

As in the tests over Pt/SiO_2 , the initial reaction products after 30 min TOS over Ru/SiO_2 were collected in a liquid nitrogen trap and analyzed by GC-MS and subsequently subjected to secondary exchange with D_2O and analyzed again by GC-MS. The results show that the ethylamine product is $\text{CD}_3\text{CH}_2\text{ND}_2$. It has its parent ion at $m/e = 50$ and a main fragmentation ion at $m/e = 32$. The diethylamine product is $(\text{CH}_3\text{CH}_2)\text{-ND-(CH}_2\text{CD}_3)$ with a molecular ion at $m/e = 77$ and fragmentation ions at $m/e = 59$, due to the loss of a -CH_3 group, and at $m/e = 62$, due to the loss of

a -CD_3 group. The butylamine product is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ND}_2$ with a molecular ion at $m/e = 75$ and a main fragmentation ion at $m/e = 42$. Butyl-ethylamine has a formula of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{-ND-(CH}_2\text{CD}_3)$; it has a molecular ion at $m/e = 105$ and fragmentation ions at $m/e = 87$, due to the loss of a -CD_3 group, and at $m/e = 62$, due to the loss of a propyl group. Diethylamine has the composition $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{ND}$; its molecular ion is at $m/e = 130$ and its main fragmentation ion is at $m/e = 87$. All the primary and secondary amines have D atoms bonded to the N atom; their mass spectra after secondary exchange with D_2O are identical with those of the fresh product.

The unsaturated Schiff base products do not react with D_2O . The MS analysis shows that ethylidene-ethylamine is mainly $\text{CH}_3\text{CH=N-CH}_2\text{CD}_3$, with a molecular ion at $m/e = 74$ and main fragmentation ions at $m/e = 56$, due to the loss of a -CD_3 group, and at $m/e = 59$ due to the loss of a -CH_3 group. The ethylidene-butylamine product is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-N=CHCH}_3$; butylidene-ethylamine is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH=N-CH}_2\text{CH}_3$. They have a molecular ion at $m/e = 99$ and fragmentation ions at $m/e = 84$ due to the loss of a -CH_3 group. Butylidene-butylamine is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-N=CHCH}_2\text{CH}_2\text{CH}_3$; it has molecular ion at $m/e = 127$ and fragmentation ions at $m/e = 113$, due to the loss of a -CH_3 group, at $m/e = 99$, due to the loss of a $\text{-CH}_2\text{CH}_3$ group, and at $m/e = 84$, due to the loss of a $\text{-CH}_2\text{CH}_2\text{CH}_3$ group.

IV. DISCUSSION

The present results show that in the co-hydrogenation of a mixture of CD_3CN and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$, a large variety of products are formed which all show the same pattern: H atoms are added to the C atoms of the CN groups, but D atoms are added to the N atoms. As the only deuterium sources are the methyl groups in CD_3CN , it is therefore unambiguously clear that an intermolecular hydrogen

transfer from the methyl groups of some acetonitrile molecules to the amine precursors on the catalyst surface takes place.

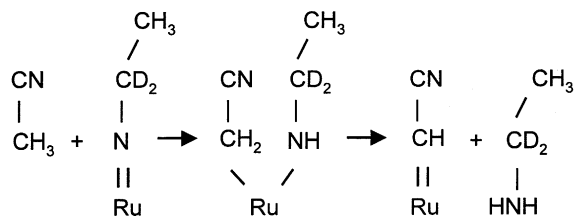
In a previous paper we reported that in the H/D exchange of amines with D₂ over the same catalysts the C-bonded H atoms were abundantly exchanged against D, but the N-bonded hydrons remained H atoms. (8) It is clear now that also in that case H transfer from the light amine to the N atom of the adsorbed intermediate took place. While this adsorbed intermediate could exchange its C-bonded H atoms against D, it was desorbed only by H-transfer to the N atom from another amine molecule. These observations and those in the present paper are reminiscent of earlier findings by Otvos *et al.* (9) that isobutane in D₂SO₄ readily exchanges all nine primary protons for deuterons but not the methine proton; the methine proton had to be specifically provided by a second isobutane molecule in a "hydride ion transfer" step.

The present data show that the methyl group in acetonitrile is much more effective as a donor of hydrons than the propyl group in butyronitrile. This might suggest some resonance stabilization in adsorption complexes of the type $M=CH-C\equiv N$ or $M\equiv C-C\equiv N$ (M = metal surface atom) resulting in a particularly easy C-H bond fission in the methyl group of acetonitrile.

Numerous literature data show that nitrile molecules can be adsorbed with both the C and the N atom of the CN group bonded to the metal surface (10-14). The analysis of our earlier isotope exchange study of acetonitrile with D₂ over Ru catalysts revealed the abundant adsorption mode of Ru=CHCN complexes. During nitrile "deuteration", i.e., the reaction $CH_3CN + D_2$, the Ru surface is covered with adsorbed $CH_3CD_2N=Ru$ groups; also in the case of Pt the metal surface is densely populated with N bonded adsorbates. In the "desorption step" strong metal-nitrogen bonds have to be broken so that amine molecules are formed. In a previous paper (1), we proposed that hydrogen transfer might be instrumental for this desorption of the amine products. That is precisely what the present results appear to confirm.

The release of a strongly held intermediate from the surface requires interaction with another impinging on weakly adsorbed nitrile molecule in accordance with the positive reaction order. This kinetics is typical for the "adsorption assisted desorption phenomenon" as studied by Yamada and Tamaru, for CO on single-crystal faces of several Pt group metals. They conclude that "reactant molecules can enhance the desorption of tightly bonded molecules in certain kinds of catalytic process." (15) The present results on nitrile hydrogenation confirm this expectation.

A simplified scheme for this unconventional chemistry is shown in Scheme 1. Ru is used as an example; its propensity to form strong N-M bonds is at the base of its ability to catalyze ammonia synthesis from N₂ and H₂.



SCHEME 1

Under the conditions of $CH_3CN + D_2$, the $CH_3-CD_2-N=Ru$ surface complex will interact with a CH_3CN molecule; H transfer leads to $CH_2-CD_2NH_2$ and $Ru=CH-CN$. The $=CH-CN$ group will pick up two adsorbed D atoms and leave the surface as CHD_2CN , so that the overall reaction, in this example, becomes



The $CH_3-CH_2-N=Ru$ surface complex can be considered the N analogue of a propylidene complex. Alkylidene complexes have been identified on metal surfaces. (16) In a previous paper (17), we have shown that secondary and tertiary amines are formed in the chemisorption layer on the metal. It is easy to see that *cis* insertion of an alkyl group to the N=bonded intermediate leads to a secondary amine, and addition of another alkyl group to the lone pair of the N atom gives the tertiary amines. This mechanism for the formation of primary, secondary, and tertiary amines appears to be in accordance with the experiment data known at the present. It provides some credence for the concept that this hydrogen transfer step is the most effective path for breaking the bond between the N atom and surface M atoms.

V. CONCLUSIONS

- (1) Intermolecular hydrogen transfer has been established by the predominant formation of deuterio nitrile groups in the co-hydrogenation of $CD_3CN + C_3H_7CN$.
- (2) The methyl group in acetonitrile is a more effective hydrogen donor than the propyl group in C_3H_7CN .
- (3) Hydrogen transfer is most efficient for breaking strong N=M bonds and *cis*-insertion of an alkyl group into an N=M bond leads to a secondary amine precursor.

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