JOURNAL OF CATALYSIS 21, 86-92 (1971)

Metal-Catalyzed Hydrogen Exchange Between Pyridine and Deuterium

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Received June 11, 1970

The hydrogen exchange reaction between pyridine and molecular deuterium has been investigated using films of Mn (62°C), Co (54–84°C), Ni (42–95°C), W (62°C), and powdered Ir (—14–101°) and Pt (100°C) as catalysis. The activities of these metals fall in the sequence Co $\sim$ Ni $\sim$ Ir $\sim$ Pt $>$ Mn $>$ W, tungsten showing very low activity under the conditions used. All of these metals catalyzed the exchange of the hydrogen atoms at positions 2 and 6 in pyridine (pair exchange). Exchange of hydrogen atoms at all positions (extensive exchange) occurred over freshly prepared Ni at 60°, Ir at 48°, and Pt at 100°C. Activity diminished when catalysts were repeatedly used; for an iridium powder the activity for the exchange of hydrogen atoms at the 3-, 4-, and 5-positions was poisoned more rapidly than the activity for exchange at the 2- and 6-positions.

Nickel film at 95°C and platinum powder at 100°C each catalyzed the hydrogenation of pyridine to piperidine.

The nickel-catalyzed exchange of 2- and of 3-methylpyridine with deuterium is reported briefly.

A mechanism for the exchange reaction is proposed.

INTRODUCTION

The metal-catalyzed hydrogenation of pyridine, quinoline, and related heterocyclic compounds has been extensively studied from the stand-point of product characterization, and the subject has been reviewed (*1*, *2*). However, there have been very few studies of the elementary processes occurring during the chemisorption of even the simplest heterocyclic compounds on metal surfaces. Consequently, the situation differs significantly from that in the field of the benzenoid aromatic hydrocarbons, where mechanisms of hydrogenation can be based on information about chemisorption obtained by the usual direct and indirect methods. For example, hydrogen exchange reactions between $C_6H_{5-x}R_x$ (R = alkyl or H) and molecular deuterium (*3*, *4*) or deuterium oxide (*5*) have provided a wealth of information (and controversy) about the nature of chemisorbed benzenes and their interaction with hydrogen.

In the heterocyclic field, Garnett *et al.* have studied hydrogen exchange between a range of nitrogen heterocycles and deuterium oxide catalyzed by all of the Group VIII metals (*6*); nickel-catalyzed pyridine exchange has also been studied by Macdonald and Shannon (*7*). Ultraviolet spectroscopy has been used recently by Kishi and Ikeda to study pyridine chemisorption on titanium, iron, and nickel (*8*).

Exchange in the liquid phase, using water as the source of the isotopic tracer has both advantages and disadvantages. The prime advantage is that it makes possible an examination of the exchange of involatile substances, and consequently a wide range of heterocyclics can be examined. However, reactions are often so slow that temperatures in the region of 100°C are normally required, and even under these conditions low conversions are sometimes reported after reaction periods of many hours or days. Furthermore, effects of the variation of temperature have not been observable.

For these reasons we considered that a

study of the metal-catalyzed hydrogen exchange reaction between pyridine and molecular deuterium using gaseous reactants would be valuable.

EXPERIMENTAL

Materials

Cobalt wire, nickel wire, iridium trichloride, and hexachloroplatinic acid were supplied by Johnson Matthey and Co. Ltd.; the wires were "Specpure" grade. Tungsten wire was supplied by the Tungsten Manufacturing Company. Manganese flake was obtained from Koch Light Ltd. Pyridine was purified by preparative glc and deuterium by diffusion through a heated palladium thimble.

Apparatus

Reactions were carried out in a grease-free high vacuum system employing mercury diffusion pumps. The Pyrex reaction vessel (250 ml) was sealed to the vacuum system by compressing an indium wire gasket between two ground glass flanges. MS3 and MS902 mass spectrometers (A.E.I. Ltd.) were used for the isotopic analysis of products.

Catalysts

Metal films were prepared according to the methods described by Kemball (*9*) involving careful outgassing of the metal and of the glass surfaces. Stocks of platinum and iridium powders were prepared by the reduction in a hydrogen stream of hexachloroplatinic acid at 274°C and of iridium trichloride at 200°C. Individual samples taken from the stocks were reduced again at 100°C for 2 hr under deuterium (100 mm Hg) and were then pumped for 30 min.

The surface areas of nickel films were measured by the deuterium chemisorption technique; typical values were about 9 m^2g^{-1}. Surface areas of iridium and platinum powders were measured by carbon monoxide chemisorption and by the oxidation of diphenylpicrylhydrazine in benzene solution (*10*); values of 7 m^2g^{-1} for iridium and of 4 m^2g^{-1} for platinum were obtained on the assumption that 50% of the carbon monoxide chemisorbed in the linear form and 50% in the bridged form.

Procedure

Reactants were mixed in the pressure ratio $C_5NH_5:D_2 = 1:10$ before admission to the vessel. The pressure of pyridine in the vessel was normally 1 or 2 mm Hg. Reactions were analyzed by one of two methods. When the powders Ir-1 and Ir-2 were investigated, the vessel was removed from the vacuum system immediately after admission of reactants and was connected to the heated inlet system of the MS902 mass spectrometer so that the reaction could be followed continuously. When the other catalysts were investigated, one analysis was made at an appropriate time during each run, usually after 30 min, using the MS3 mass spectrometer (cold inlet system). Great care was taken to ensure that the MS3 was clean before samples were examined, otherwise traces of previous pyridine samples were displaced from the walls of the cold inlet system, and constituted an intolerable contamination. Spectra were obtained at 12 eV; no appreciable fragmentation of pyridine occurred. Corrections were applied to take account of naturally occurring carbon-13 and deuterium.

RESULTS

Hydrogen exchange between pyridine and deuterium occurred at the surfaces of all of the metals studied, whereas hydrogenation to piperidine was observed only over nickel and platinum at about 100°C.

The course of the exchange reaction was investigated in detail over iridium powder at −14°C (sample Ir-1) and at 19°C (sample Ir-2). The results are shown in Figs. 1(a) and 2(a), respectively. At the lower temperature two hydrogen atoms are rapidly exchanged for deuterium, whereas at the higher temperature all the hydrogen atoms exchanged at a measurable rate.

Some 50 exchange reactions were carried out for each of which one analysis only was made; a selection of typical results is shown in Table 1. The exchange of two

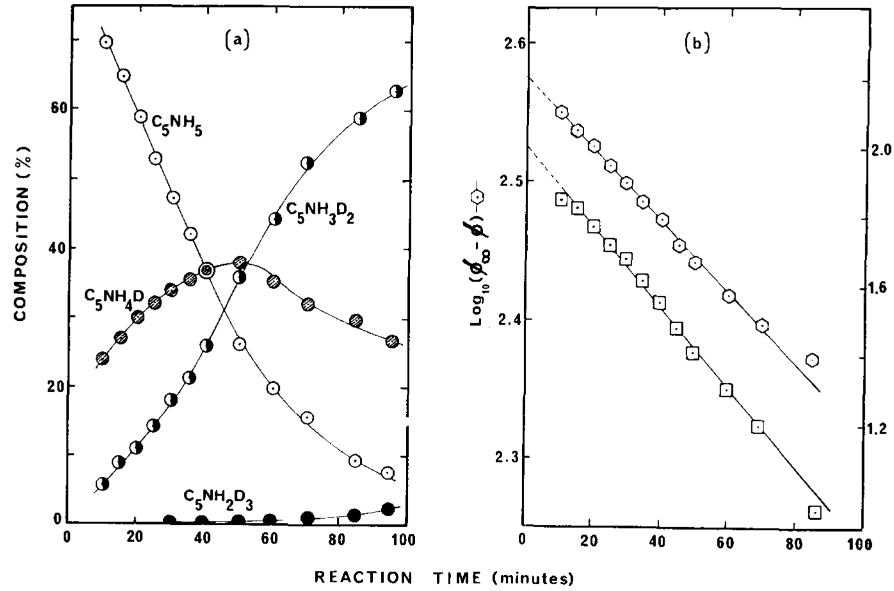

FIG. 1. (a) The variation of the composition of the reaction mixture with time over Ir-1 (an iridium powder weighing 49.6 mg.) at −14°C. (b) The function plots for reaction over Ir-1, where $\phi = \Sigma_{i=1}^{i=5} i[d_i]$ where d_i is the percentage of pyridine containing i deuterium atoms.

hydrogen atoms for deuterium was the major process over nickel films at 42°C, cobalt films in the range 54–84°C, and manganese and tungsten films at 62°C. NMR analysis of products obtained over nickel showed that exchange had occurred in the 2- and 6-positions, i.e., at the positions *ortho* to the nitrogen atom. However,

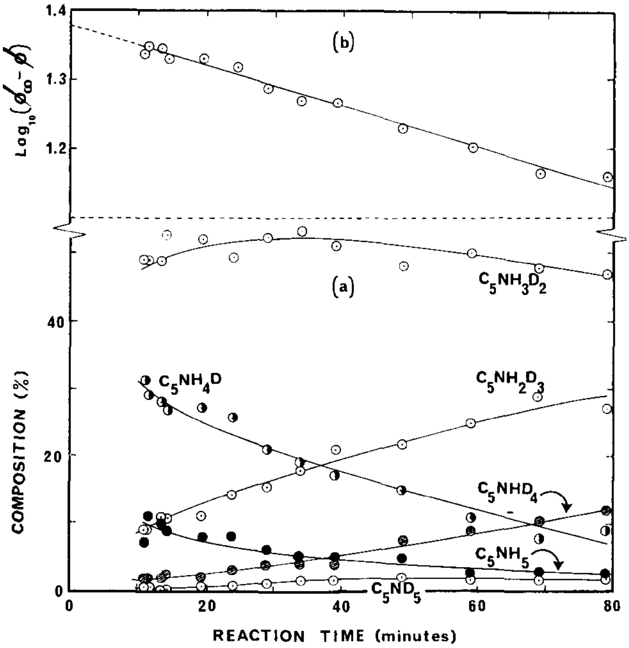

FIG. 2. (a) The variation of the composition of the reaction mixture with time over Ir-2 (an iridium powder weighing 49.0 mg.) at 19°C. (b) The function plot for reaction over Ir-2.

TABLE 1
PRODUCTS OF THE HYDROGEN EXCHANGE REACTION BETWEEN PYRIDINE AND DEUTERIUM CATALYZED BY VARIOUS METAL FILMS AND POWDERS

Catalyst	Weight (mg)	Temp. (°C)	Reaction time (min)	Products (%)						
				C_5NH_5	C_5NH_4D	$C_5NH_3D_2$	$C_5NH_2D_3$	C_5NHD_4	C_5ND_5	ϕ
Ni-film	4.7	42	30	11	9	79	1	0	0	167
Ni-film	11.7	60	30	10	9	71	6	3	1	151
Ni-film	10.3	95	30	25	15	25	24	11	0	181
Co-film	11.8	65	30	23	8	68	1	0	0	144
Mn-film	46.8	62	30	53	4	43	0	0	0	90
W-film	12.1	58	30	96	0	4	0	0	0	8
Ir-3-pwdr	19.8	0	15	55	27	17	1	Tr[a]	0	64
Ir-4-pwdr	20.0	25	15	18	28	51	3	Tr[a]	Tr[a]	139
Ir-5-pwdr	20.2	48	30	7	4	30	35	19	5	270
Pt-pwdr	100	100	30	7	11	58	19	4	1	205

[a] Tr = trace (0.1 to 0.4%).

as the temperature of the nickel-catalyzed reaction was raised, the exchange of three and of four hydrogen atoms was observed. Furthermore, analysis by mass and NMR spectrometry revealed that considerable hydrogenation to piperidine had taken place at 95°C.

Results obtained using the iridium powders Ir-3, 4, and 5 confirm those reported in Figs. 1(a) and 2(a). Again the extent of the exchange clearly increases with increasing temperature. Platinum powder at 100°C catalyzed the exchange of up to five hydrogen atoms but the exchange of a set of two was again the most rapid process taking place. Exchange was accompanied by hydrogenation to piperidine.

A series of ten exchange reactions was carried out using the powder Ir-5, to examine whether the exchange pattern changed as the catalyst was used. A selection of the results is shown in Table 2. Clearly, activity for the exchange of five hydrogen atoms diminished rapidly so that, by the ninth reaction, exchange was confined to a set of two hydrogen atoms even at 101°C. Furthermore, comparison of Ir-5 run 3 with Ir-4 run 1, or of Ir-5 run 7 with Ir-3 run 1 shows that the activity for the exchange of two hydrogen atoms in pyridine also diminished as the catalyst was used.

The exchange of 2- and of 3-methylpyridine with deuterium was examined briefly using nickel films (3–20 mg) at 42°C. After 30 min, the 2-methylpyridine had attained the composition $C_6NH_7 = 14\%$, $C_6NH_6D = 64\%$, $C_6NH_5D_2 = 12\%$, $C_6NH_4D_3 = 5\%$, $C_6NH_3D_4 = 5\%$. More highly exchanged products were not observed. The exchange

TABLE 2
PRODUCT COMPOSITIONS OBSERVED IN A SERIES OF REACTIONS CATALYZED BY IRIDIUM-5 POWDER[a]

Experiment number	Temp. (°C)	Reaction time (min)	Products (%)					
			C_5NH_5	C_5NH_4D	$C_5NH_3D_2$	$C_5NH_2D_3$	C_5NHD_4	C_5ND_5
1	48	30	7	4	30	35	19	5
3	28	15	46	24	22	3	2	3
7	0	15	85	10	4	1	Tr[b]	Tr[b]
9	101	15	53	24	22	1	Tr[b]	0

[a] Catalyst weight = 20.2 mg.
[b] trace = 0.3 %.

of 3-methylpyridine was confined to the formation of C_5NH_6D.

Discussion

The Multiplicity of the Exchange

Inspection of Fig. 1a shows that exchange was stepwise over Ir-1 at −14°C. The results have been evaluated using Kemball's procedure (*11*, *12*). The appropriate function plots (Fig. 1b) are linear, and the ratio of the gradients gives a value of M (the mean number of hydrogen atoms replaced by deuterium in each molecule of pyridine undergoing exchange in the initial stages of reaction) of 1.0 ± 0.1. This confirms that exchange is stepwise. A reliable value of M cannot be obtained for the reaction over Ir-2 at 19°C because too large a proportion of the C_5NH_5 was consumed before analysis commenced.

The intercept of Fig. 1(b) gives a value of ϕ_∞ that is close to the expected value of 388. However, the intercept of Fig. 2(b) has a much lower value, indicating that the reaction was proceeding in two stages, the first being exchange at the 2- and 6-positions (which was almost complete by the time the analyses commenced) and the second being the incorporation of deuterium into the remaining positions. The rate constant of the latter process is obtainable from the gradient of the line in Fig. 2(b).

The linearity of Figs. 1(b) and 2(b) also demonstrates that poisoning did not occur during the course of a reaction.

Rate constants and values of M based on single analyses are inherently unreliable. However, for the reactions reported in Tables 1 and 2, the values were in the range 1.0–1.3 for reactions over nickel at 42 and 60°C, cobalt at 65°C, fresh iridium powders at 0 and 25°C, and platinum powder at 100°C. Higher values, in the range 1.7–2.0 were recorded for fresh iridium powder at 48°C and for the manganese and tungsten films at about 60°C.

Definitions

In the discussion of mechanism that follows the term *pair exchange* will be used to denote the process whereby the hydrogen atoms at the 2- and 6-positions are exchanged for deuterium atoms, and the term *extensive exchange* will denote the processes which enable all five hydrogen atoms in pyridine to undergo exchange.

Mechanism of the reaction. The chemisorption of pyridine on nickel films at ambient temperatures has been examined using ultraviolet spectroscopy by Kishi and Ikeda (*8*). This investigation shows that chemisorption is achieved by the formation of a coordinate bond between the nitrogen atom of pyridine and a metal atom (or site) at the surface. The observation of fine structure in the spectrum of the chemisorbed pyridine led to the conclusion that there is little or no π-interaction between the delocalized electrons of the aromatic ring and the surface. This species is shown as (I) in Fig. 3. (I) is among the chemisorbed species proposed by Garnett *et al.* to account for the hydrogen exchange reaction between pyridine and heavy water (*6*).

Chemisorption of pyridine as (I) allows a ready understanding of hydrogen exchange at positions 2 and 6, since the hydrogen atoms in question are those most closely situated to the surface. Such an exchange may proceed by an addition-abstraction mechanism as shown in Fig. 4, or by an abstraction-addition mechanism involving species (I) and (II) shown in Fig. 3. In either case, $M = 1$ if pyridine desorption is rapid in comparison with the rate of the exchange process, and $M = 2$ if the reverse is the case.

A choice between these mechanisms may be made by considering the exchange of 2- and of 3-methylpyridine with deuterium. The substitution of the hydrogen atom at the 2-position for a methyl group should confine the exchange to that in the 6-position only if the addition-abstraction mechanism is operative. However, the hydrogen atoms of this methyl group are in very close proximity to the surface, and hence the abstraction-addition mechanism may accomplish the exchange of the hydrogen atoms of the methyl group as well as the hydrogen atom at the 6-position.

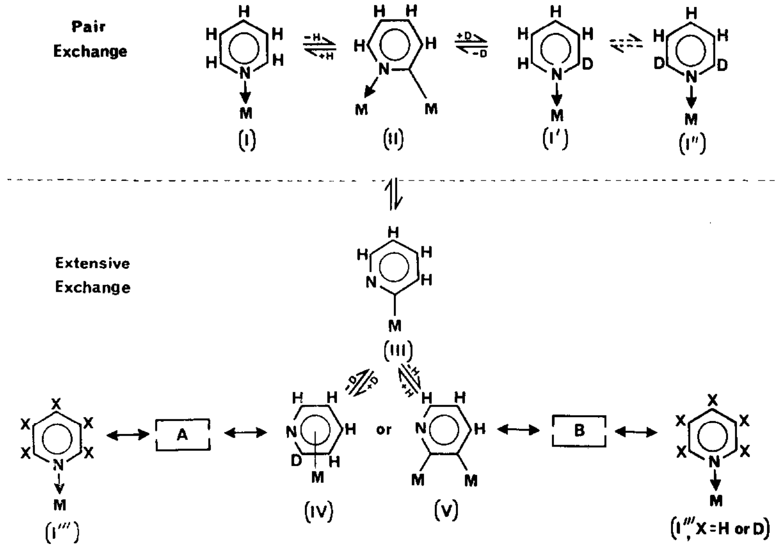

FIG. 3. An abstraction-addition mechanism for pair exchange, and a mechanism for extensive exchange.

The experimental observation, using a nickel film under pair-exchange-only conditions, is that up to four hydrogen atoms exchanged; this is consistent with reaction by the abstraction-addition process. Consequently, the mechanism in Fig. 3 for pair exchange in pyridine is the more likely of the two alternatives.

On this basis, pair exchange was expected in the reaction of 3-methylpyridine.

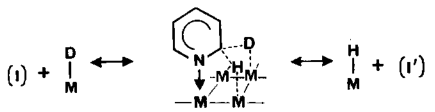

FIG. 4. An addition-abstraction mechanism for pair exchange.

The observation that only one hydrogen atom was exchanged may indicate that exchange of the other was sterically hindered by the methyl group.

The extensive exchange observed over nickel at 95°C, Ir-2 at 19°C, Ir-5 at 48°C and platinum at 100°C shows that further chemisorbed species are formed at these surfaces at sufficiently high temperatures. Garnett *et al.* (*6*) have proposed that, when extensive exchange occurs, the chemisorption of pyridine involves not only chemical bonding as in (I) but also an interaction between the π-electrons of the aromatic ring and the surface that is sufficiently strong to bring the hydrogen atoms at positions 3, 4, and 5 into close proximity with the surface. The present work has shown that nickel and iridium give extensive exchange at temperatures only thirty degrees or so higher than those at which reaction is almost entirely limited to pair-exchange. Consequently, the difference between pair-exchange and extensive exchange in these cases is unlikely to be due to anything as fundamental as the mode of the initial chemisorption of pyridine. It is more likely that the critical increase in temperature alters the reactivity of some intermediate. Consider species (II) of Fig. 3 in this context. An increase in temperature is expected to enhance the rate of rupture of the metal-nitrogen bond, just as it is expected to increase the rate of pyridine desorption. Consequently, the rate of conversion of (II) to (III) will increase with increasing temperature. Species (III) is admirably suited to initiate extensive exchange on several counts. First, it is analogous to σ-adsorbed phenyl which is a proposed species in the dissociative π-complex substitution mechanism for benzene exchange (*6*). Secondly, by conversion to (IV) it becomes analogous to π-adsorbed benzene, and extensive exchange could occur by processes analogous to the associative π-complex substitution mechanism for benzene exchange (*4*). These processes (which are discussed in detail in reference 6) are represented by box A in Fig. 3. Thirdly, extensive exchange could occur involving the two possible α-β di-σ-adsorbed species; this process is represented by box B in Fig. 3. No choice between these alternatives can be made at present. Nevertheless, there is a *prima facie* case for supposing that the conversion of (II) to (III) is the critical step in the initiation of extensive exchange.

Organic nitrogen bases such as pyridine and quinoline are noted poisons for metal-catalyzed hydrogenation reactions (*13*) and it is commonly supposed that the base is chemisorbed irreversibly at a proportion of the surface sites. Consequently, the progressive deactivation observed when ten pyridine exchange reactions were carried out over Ir-5 is not remarkable. It is surprising, however, that activity for extensive exchange is poisoned more rapidly than activity for pair exchange. This may be analogous to Crawford and Kemball's reports (*12*, *14*) of the disproportionate effect of sintering and of carbon monoxide chemisorption on the rate of ring exchange in toluene over nickel films in comparison with its effect on the rate of side-chain exchange. The poisoning is not progressive with extent of reaction (see linearity of Figs. 1b and 2b). This shows that a slowly accumulating quantity of pyridine is irreversibly chemisorbed and that it is not the reaction itself that produces the poison.

Finally, we compare briefly the present work with the results of liquid phase reactions at 130°C reported by Garnett *et al.* (*6*) in which deuterium oxide was the source of the isotope. These workers also observed extensive exchange of pyridine over nickel and platinum, but only with a proportion of their catalysts, the remainder of which gave pair exchange. Cobalt was found to be very selective for pair exchange, as we have observed. There is a substantial point of difference in that these workers report iridium to possess low pair exchange activity, whereas the iridium catalysts used in this work were highly active for extensive exchange even at room temperature. These disparities merely emphasize the need for further examination of this reaction; indeed, it may well be that the majority of these metals will exhibit pair exchange at low temperatures and extensive exchange at higher temperatures provided their surfaces are substantially free of poisons.

ACKNOWLEDGMENTS

We acknowledge the assistance of Messrs. L. W. Cheriton, R. G. Oliver, K. Robinson, and Miss M. M. Taylor with the experimental work. The mass spectrometers were purchased with the aid of grants from the Science Research Council (MS902) and the former Department of Scientific and Industrial Research (MS3).

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