

NOTE

Hydrogenolysis and Deuterium Exchange of C₃ and C₄ Primary Alkylamines Catalyzed by Platinum Films

Studies by Kemball and Moss (1, 2) established that on platinum catalysts the vapours of the simplest primary amines RNH_2 readily underwent hydrogenolysis. Earlier work (3) showed that at temperatures below 273 K, platinum catalyzed the exchange of deuterium with the amine hydrogens only. This suggests that adsorption of an alkylamine molecule on a platinum catalyst involves, initially, the interaction of the amine group, probably in a process of dissociative adsorption.

Subsequent studies (4) with cyclohexylamine, where benzene was an initial product, support the view that, prior to the dissociation of the C-N bond, the alkyl end of the molecule is substantially chemisorbed to the surface. On this basis, it appears that the hydrogenolysis of the amine RNH_2 , where the alkyl radical R is either primary or secondary, involves the participation on the surface of a species in which both the N and the neighbouring C atom are involved in chemisorption to the catalyst surface. The question then arises as to what will happen if R is a tertiary radical, where chemisorption in the manner described above would require C-C bond fission. It was considered prudent to compare the behaviour of *tert*-butylamine on platinum with that of other C₃ and C₄ amines, involving both primary and secondary alkyl radicals.

The apparatus employed a demountable reaction vessel linked as in the previous work (1-4) by a capillary leak to an MS10 mass spectrometer, operated in the latter part of the work by an RGA-10 control unit. Platinum films of ca. 10 mg, covering an area of ca. 70 cm², were evaporated by a routine similar to that used in the earlier

work. The film was maintained at ice temperature until the reaction mixture was expanded into the reaction vessel.

BDH laboratory reagent-grade alkylamines were used. Before each experiment a sample of the relevant amine was put on the vacuum line and degassed by five cycles of freeze-pump-thaw. Mixtures were made up in a mixing space using the vapour from this sample along with 99.5% pure hydrogen or deuterium. Reagent-grade hydrocarbons and ammonia were used for calibrations.

In the experiments with 1-propylamine, the amine was monitored using the parent peak at $m/e = 59$ and the more abundant fragment ion at $m/e = 30$. For the other amines, as shown in the published fragmentation patterns (5), the parent peaks are not sufficiently abundant. 2-Propylamine and 2-butylamine were monitored using $m/e = 44$ and 18, respectively, due to the ions $C_2NH_6^+$ and NH_4^+ , and 1-butylamine using $m/e = 30$, due to CNH_4^+ . For decomposition reactions, *tert*-butylamine was monitored at $m/e = 41$ and 58, due to the ions $C_3H_5^+$ and $C_3NH_7^+$. Because of insufficient resolution at the latter mass number, the deuterium exchange reaction was monitored using $m/e = 30$ and 18. Ammonia was followed at $m/e = 17$, propane at $m/e = 43$ and 29, *n*-butane and isobutane at $m/e = 43$. For each experiment, the electron-accelerating voltage was chosen so as to effect a compromise between peak size and excessive fragmentation. For parts of the work, 30 V was found suitable. For the hydrogenolysis reactions, calibrations of the mass spectrometer sensitivity were made using authentic mixtures of the reactants and

products. In evaluating rates of reaction, allowance was made for the increase in peak size with increasing temperature of the reaction vessel.

In all cases, when a mixture of an alkylamine plus hydrogen was admitted to a freshly prepared film of platinum in the reaction vessel, no reaction was observed until the catalyst temperature was raised above 400 K, when the 17 peak due to ammonia was seen to rise along with that due to the alkane RH, and those due to the alkylamine decreased. Since ammonia and alkylamines are strongly adsorbed on the inlet system of the mass spectrometer (3, 6, 7), the changes in the alkane peaks were considered more accurately indicative of the rate of the reaction than those of the peaks due to these polar compounds.

The reactivity of each amine toward catalytic hydrogenolysis was measured using a standard mixture which, when first admitted to the reaction vessel, gave 10.7 Torr amine and 43.0 Torr H₂ (where 1 Torr = 133.3 N m⁻²). With the amines other than *tert*-butylamine, this reaction was invariably observed at 423 K, at rates in the range 0.4 to 0.9% of the amine per minute, showing variations which could be partially attributable to differences in the actual surface areas of the films. With *tert*-butylamine, no reaction was observed below 473 K, where a rate of ca 0.3% min⁻¹ was observed, which rose to 1.9% min⁻¹ at 523 K. Thus the hydrogenolysis of *tert*-butylamine was significantly slower than that of the other amines, under the same conditions.

In the light of previous work (7) using films of metals such as platinum, it was assumed that at the reaction temperatures the actual surface is just a few times greater than the area of vessel covered by the film. This is essentially constant in these experiments, so no correction was made for the slight variations in the weight of the platinum films in different experiments.

With 1-propylamine, 2-propylamine, and *tert*-butylamine, additional experiments

were carried out with a much higher pressure of hydrogen. In all cases, slower reaction was observed, leading to negative formal reaction orders with respect to H₂, especially for *tert*-butylamine.

When a mixture of an alkylamine vapour and D₂ was admitted to a platinum film at 273 K, peaks appeared corresponding to the gradual formation of first the *d*₁ and then the *d*₂ amine. Since there were no peaks corresponding to the *d*₃ amine and since at all times the relative sizes of the three peaks were such that $[d_1]^2/([d_0][d_2]) = 4$, within experimental error, it was clear that only the amine hydrogens were participating in this deuterium exchange. This concurs with the conclusion from earlier studies (3) of simple alkylamines on platinum.

It was also found, using 1-butylamine, that when a mixture of RNH₂ along with an equilibrium mixture of RNH₂, RNHD, and RND₂ was put into the reaction vessel, with no catalyst present, at all times the mass spectrometer showed peaks for the *d*₀, *d*₁, and *d*₂ amines such that, within experimental error, $[d_1]^2/[d_0][d_2] = 4$. This was attributed to the memory effect (3, 6) of the mass spectrometer, and to the re-equilibration of the amines analogous to the known behaviour of ammonia (8).

Since we found it impossible to observe a distribution of deuterio-amines other than the equilibrium one, it would not seem justified to assert that the exchange with deuterium of the amine hydrogens must take place one at a time. Such a mechanism would certainly lead to a *d*₀ : *d*₁ : *d*₂ distribution the same as that which was observed, but it would appear that the apparatus must show this same result even if both amine H atoms were replaced by D in the catalytic process on the platinum surface. The only warranted conclusion is that the amine hydrogens undergo exchange with deuterium.

When a mixture of 1-propylamine and D₂ was admitted to a platinum catalyst at 273 K, partial exchange of the amine hydrogens occurred. When the temperature was in-

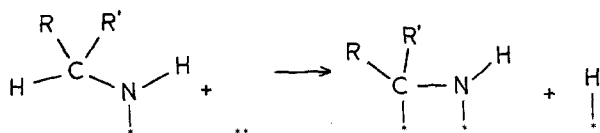
creased step-wise, further exchange of the amine group was observed at 330 K. At 388 K, with the d_2 isomer more abundant than the d_1 , the peak corresponding to the d_3 isomer was observed, rising very slowly. Multiple exchange also occurred at 430 K, at which temperature the amine was decomposing to ammonia and propane.

The behaviour of 2-propylamine was virtually identical to that described above. With 2-butylamine, exchange of the amine hydrogens occurred at 273 K, and readily at 350 and 375 K, with the d_3 compound only appearing after 40 min at the latter temperature. At 423 K, there occurred both further exchange and decomposition of the amine. With 1-butylamine, exchange of the amine

hydrogens occurred at 273 and 323 K, rather slowly.

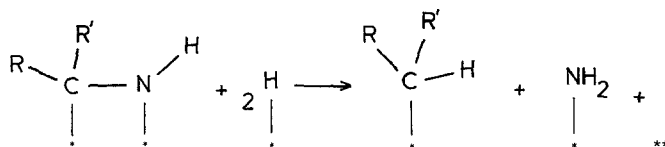
With *tert*-butylamine, exchange was limited to the amine hydrogens at 273, 333, and 373 K. Additional exchange, producing the d_3 compound, was detected at 433 K, where slow decomposition was also occurring.

The nature of the deuterium exchange pattern shown by these alkylamines suggests that an amine molecule can be chemisorbed on a platinum surface at 273 K, with involvement of the amine moiety. At higher temperatures most amines also show exchange within the alkyl group, which would seem to imply that there is some form of chemisorption involving, additionally, the alkyl group. Where the alkyl group is not a tertiary one, one may suggest the process



Desorption of such a species can lead to a D atom on the alkyl group. The near coincidence of the conditions for alkyl group ex-

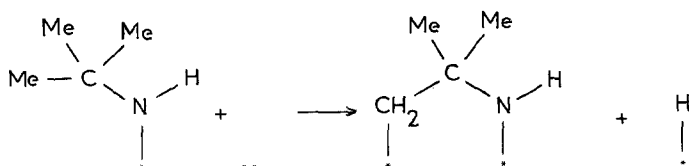
change and hydrogenolysis suggests that the same adsorbed species could be involved in the two processes.



The inverse dependence of the rate of hydrogenolysis on hydrogen pressure is consistent with this proposal.

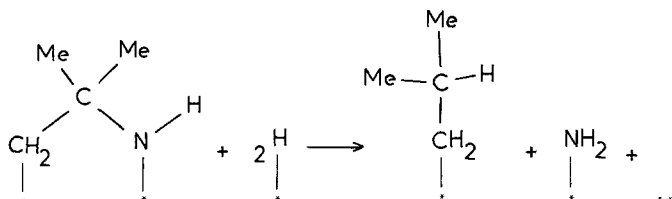
With *tert*-butylamine, the pattern of exchange is essentially the same and a similar adsorbed intermediate may be invoked. However, *tert*-butylamine does not show

any exchange of the alkyl H atoms until ~433 K. It would seem inevitable that this process involves another adsorbed species and, given the structure of this molecule, this may well be an α,γ -diadsorbed species analogous to that invoked (9) in the deuterium exchange of neopentane.



The fact that the conditions for exchange of alkyl H atoms nearly coincide with those of hydrogenolysis both exacerbates the problems of studying this exchange in more detail and also suggests that mechanistically the two processes may have some-

thing in common. The decomposition of *tert*-butylamine yields, in addition to ammonia, isobutane and not propane, so it would seem probable that the chemisorbed species involved in the hydrogenolysis is that depicted below:



The finding that the hydrogenolysis of *tert*-butylamine is inhibited by hydrogen to a greater extent than the other amines is not fully explained by the above proposals, but it would seem to reflect the occurrence of this reaction by a different mechanism involving a distinct adsorbed intermediate.

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