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Catalyzed Deuterium Exchange and Decomposition Reactions of Methylhydrazine and 1,1-Dimethylhydrazine on Transition Metals

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A study of the catalytic exchange with deuterium of methylhydrazine and 1,1-dimethylhydrazine shows that, on films of palladium and platinum, the hydrazyl hydrogens exchange at around room temperature. At higher temperatures decomposition of each alkylhydrazine occurs, mostly if not entirely by N–N bond fission. On nickel, some deuterium exchange is seen, apparently of the hydrazyl hydrogens, at temperatures where decomposition is also occurring. No exchange was observed on iron on which decomposition occurred readily and on tungsten a small extent of exchange was seen only of 1,1-dimethylhydrazine, which does not decompose so readily. On palladium the two exchange reactions show different formal orders with respect to deuterium. In almost all cases, increased hydrogen pressure decreases the rates of the decomposition processes, presumably by inhibiting the formation of the requisite diadsorbed species.

INTRODUCTION

Some years ago, various deuterium exchange studies were conducted, particularly by Kemball and co-workers (*1*, *2*), on the behaviour of a range of amino-compounds on catalyst surfaces. In the case of methylamine, for example (*1*), these showed that individual transition metals tended to catalyze the deuterium exchange of either the methyl or the amine hydrogens, at temperatures well below those where C–N bond rupture occurred (*2*). Such findings have obvious implications regarding the manner in which the molecule is adsorbed on each transition metal.

It was thought desirable to apply the same technique to look at the molecules methylhydrazine and 1,1-dimethylhydrazine, where comparable questions arise. One might surmise that, on different transition metals, the tendency for one or other group (i.e., hydrazyl or methyl) of hydrogen atoms to undergo exchange is closely correlated with the respective exchange rates exhibited by ammonia and methane.

In the case of methylhydrazine there is the additional issue as to whether all three nonequivalent hydrazyl hydrogen atoms undergo exchange with equal ease. With ammonia, where all the hydrogen atoms are equivalent, it follows from the symmetry numbers that for the equilibria

$$d_0 + d_2 \rightleftharpoons 2d_1$$

and

$$d_1 + d_3 \rightleftharpoons 2d_2,$$

in each case the equilibrium constant $K = 3$ (d_i signifies a molecule with i deuterium atoms). For methylhydrazine it can be shown that these same values apply, provided one assumes that the same proportion of the H atoms are exchanged in the –NH– group as in the $-NH_2$ group, which requires that the H atoms all undergo exchange with equal facility. The case of 1,1-dimethylhydrazine is entirely analogous to that of an alkylamine and from the symmetry numbers we have $K = 4$ for the equilibrium,

$$d_0 + d_2 \rightleftharpoons 2d_1.$$

Various studies have been carried out (*3–6*) on the catalytic decomposition of hydrazine vapour on transition metals. One of these (*5*) also reported that hydrazine under-

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went catalytic exchange with deuterium on palladium at room temperature. In general, ammonia and nitrogen are both found as decomposition products, even in cases where the presence of excess hydrogen would permit simple hydrogenolysis to occur to yield ammonia only. Studies of the decomposition of 1,1-dimethylhydrazine over supported metal catalysts (*7*) indicate the presence of two pathways, one leading by N–N bond rupture to dimethylamine and ammonia, and the other, by C–N bond rupture, to methane and N_2.

In the course of the exchange studies it was found that these alkylhydrazines undergo catalytic decomposition at temperatures not far above those required for deuterium exchange. It was decided to study also the kinetics of the former reaction, so that the relevant evidence from both processes could be used to deduce the manner in which the molecule is adsorbed on the surface.

EXPERIMENTAL

The apparatus and techniques were similar to those used in previous work (*8*), and employed an MS10 mass spectrometer to monitor the contents of the reaction vessel, continually sampled by a capillary leak. Films of the various metals employed were prepared as described earlier (*9*), with the reaction vessel in an ice-bath.

Aldrich 98% grade methylhydrazine and 1,1-dimethylhydrazine were used without further purification. Samples of each were put on the vacuum line and degassed by five cycles of freeze–pump–thaw. Reaction mixtures were made up using the respective vapour along with 99.5% pure hydrogen or deuterium, and were expanded into the reaction vessel, still held at 273 K, just after the film had been prepared.

A sample of anhydrous hydrazine was prepared, for calibration purposes, via the compound $C_6H_4(CO)_2NNH_2 \cdot N_2H_4$ (*10*), which yields the former by thermal decomposition when heated under vacuum. When a sample of hydrazine vapour, along with hydrogen, was admitted to the reaction vessel, the only peaks seen were those expected from N_2 and NH_3: no peak was seen at $m/e = 32$ corresponding to the parent ion, $N_2H_4^+$. This finding is in contrast to the reported mass spectral data on hydrazine (*11*, *12*) but is consistent with previous observations using an instrument with a Nier-type source or in earlier work using the MS10 spectrometer.

When a sample of either methylhydrazine or 1,1-dimethylhydrazine, with some hydrogen, was put into the reaction vessel with no film present, there was, in each case, good correspondence between the peaks seen and those listed by Dibeler *et al.* (*12*). However, as reported by those authors, peaks were also seen corresponding to rearrangement products, e.g., $m/e = 27$ due to HCN^+. Over a period of time a gradual decrease in the size of the parent peaks was seen, of the order of ca. 12% per hour for each compound, with a concomitant rise in the $m/e = 17$ (NH_3^+) peak and that at $m/e = 31$ ($CH_3NH_2^+$) or 45 ($(CH_3)_2NH^+$) corresponding to the other product of N–N bond hydrogenolysis. It was shown that these changes in peak height were entirely due to the behaviour of the respective alkylhydrazines in the MS10 mass spectrometer and were not caused by processes within the reaction vessel catalyzed by the tungsten leads. However, their existence meant that a decrease in the size of the parent peaks of either reactant was significant only to the extent by which it exceeded the value quoted above.

For the deuterium exchange studies, an electron energy of 14 eV was found suitable for the mass analysis. Where exchange occurred, it was found to stop at three atoms in the case of methylhydrazine and two atoms in the case of 1,1-dimethylhydrazine, which suggested that it was the hydrazyl hydrogens which were participating. At 14 eV, the fragment ion peaks, at $m/e = 45$ and 59, respectively, both corresponding to the loss of H, were substantial and corrections were necessary to all peaks except that at the highest m/e observed. These were made on the assumption that the fragments are formed by loss of a methyl H atom, an assignment which seemed to fit the data. From the calculated amounts d_i of the molecule with i atoms of deuterium, the dimensionless parameter ϕ was calculated.

$$\phi = \sum_{i=1}^{n} id_i \Big/ \sum_{i=0}^{n} d_i.$$

Plots of $\ln(\phi_\infty - \phi)$ against time were then used to evaluate the rate constant for deuterium exchange and, assuming surface area proportional to film weight, were then adjusted to obtain the value for a film of 10 mg.

In all cases, decomposition reactions were found to be first order with respect to the alkylhydrazine, under conditions of excess hydrogen. Where the rate of decrease of the parent peak was appreciable, this was used to evaluate the first-order rate constant. To find the reaction order with respect to hydrogen, another run at a different hydrogen pressure was performed on the same catalyst. To minimise catalyst sintering between runs, the reaction vessel was cooled in an ice-bath before the first reaction mixture was pumped out.

RESULTS

Palladium

When a mixture of methylhydrazine vapour and D_2 was admitted to a fresh palladium film at 273 K, deuterium exchange to produce the d_1, then the d_2, and finally the d_3 compound was seen to occur. It seemed that, at all stages, the ratio, d_1^2/d_0d_2 was, within experimental error, equal to 3, which implies the equilibrium, $2d_1 \rightleftharpoons d_0 + d_2$. From the later stages of the reaction, there was similar evidence of the equilibrium, $2d_2 \rightleftharpoons d_1 + d_3$.

Similarly, on a palladium film at 273 K, deuterium exchange occurred with 1,1-dimethylhydrazine to produce first the d_1 and then also the d_2 compound, with the ratio d_1^2/d_0d_2 equal, within experimental error, to 4 which implies the equilibrium, $2d_1 \rightleftharpoons d_0 + d_2$.

In both cases, more rapid exchange occurred when the temperature of the palladium catalyst was raised, giving good linear plots of $\ln(\phi_\infty - \phi)$ against time which indicated an absence of self-poisoning. For methylhydrazine the ratio of the rate constants gave an apparent activation energy of 27 ± 4 kJ mol^{-1}. In the case of 1,1-dimethylhydrazine the corresponding value was around 20 kJ mol^{-1}.

To evaluate the kinetic order of the exchange reaction with respect to D_2, series of runs were carried out in which the partial pressure of the alkylhydrazine was kept constant while that of D_2 was varied. The relevant general equation has been shown (*13*) to be

$$\ln \phi_\infty - \ln(\phi_\infty - \phi) = \frac{k_n(a + b)t}{a^{1-p}b^{1-q}} = k't, \qquad (1)$$

where a and b represent the initial concentrations of the reacting species of respective reaction orders p and q. This equation shows that whereas the approach to equilibrium in any individual experiment follows pseudo-first-order behaviour, the pseudo-first-order rate constant k' derived from the negative gradient of the plot of $\ln(\phi_\infty - \phi)$ against t depends on the concentrations of the reacting species and on their actual reaction order. Thus where b is kept constant, a plot of $\ln(k'/(a + b))$ against $\ln a$ should have a slope of $(p - 1)$.

Figure 1 shows the relevant plots of $\ln(k'/(a + b))$ against $\ln p_{D_2}$, where the k' values had been adjusted to those of a film of 10 mg. Equating the gradients to $(p - 1)$, we obtain values of 0.65 and -0.1 for the order with respect to D_2 in the respective exchange reactions of methylhydrazine and 1,1-dimethylhydrazine.

Above ca. 320 K, the peaks due to methylhydrazine were found to decrease more rapidly, with a corresponding rise in those due to ammonia and methylamine. Similar decomposition of 1,1-dimethylhydrazine was seen above ca. 360 K, leading to ammonia and dimethylamine. It was found, in experi-

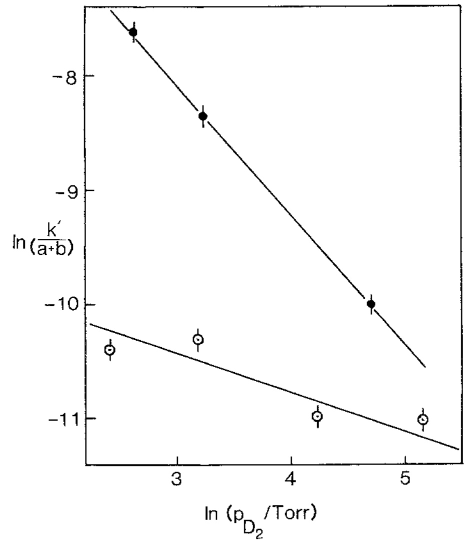

FIG. 1. Plots of $\ln k'/(a + b)$ against $\ln p_{D_2}$ for the exchange reactions, on 10-mg films of palladium at 273 K, of methylhydrazine (○) at a pressure of 16 Torr and 1,1-dimethylhydrazine (●) at 22 Torr.

ments using D_2, that at around 455 K up to the d_5 isomer of dimethylamine could be seen, indicating exchange of the methyl hydrogens under conditions where the dimethylamine was also decomposing. In the course of the latter process, trimethylamine was seen to be produced.

By comparing the rates of decomposition of methylhydrazine at two different (excess) hydrogen pressures on the same film, the reaction order with respect to hydrogen was found to be -0.8, which indicates inhibition. For 1,1-dimethylhydrazine the exponent was found to be -1.2, with the same implication. The latter reaction yielded an apparent activation energy of ca. 65 kJ mol^{-1}.

Platinum

Exchange of the alkylhydrazines with deuterium occurred in a very similar manner on platinum films, with exchange apparently confined to the hydrazyl hydrogens and the various deutero-compounds in equilibrium. Exchange of each compound occurred readily at 273 K and from the effect of a 50 K rise in temperature, apparent activation energies were deduced as ca. 32 kJ mol^{-1} ($MeNHNH_2$) and ca. 18 kJ mol^{-1} (Me_2NNH_2).

Above ca. 300 K, there was clear evidence of the decomposition of methylhydrazine by N–N bond rupture. For the decomposition reaction the apparent activation energy was ca. 46 kJ mol^{-1} and the order of reaction with respect to H_2 was -0.5. The other alkylhydrazine decomposed in much the same temperature range to give dimethylamine but on platinum trimethylamine was not detected. In the presence of D_2, multiple exchange of dimethylamine was found, implying exchange of the methyl hydrogens.

Nickel

Over a nickel catalyst, methylhydrazine showed no exchange at 273 K, but exchange could be detected above ca. 320 K, producting the d_1 and d_2 products. A value of ca. 40 kJ mol^{-1} was obtained as the apparent activation energy of the exchange process, which tended to be accompanied by decomposition to methylamine and ammonia. The latter reaction, with an apparent activation energy of ca. 60 kJ mol^{-1} became relatively more important at higher temperatures. Studies using two different pressures of H_2 on the same film yielded an exponent of -1.0 with respect to H_2.

Similarly, 1,1-dimethylhydrazine showed no perceptible exchange with D_2 on nickel at ice temperature but above ca. 310 K exchange of up to two hydrogen atoms was seen. The apparent activation energy found for this process was ca. 18 kJ mol^{-1}, but the extent of the decomposition reaction occurring at the upper temperature probably makes it unreliable despite the good linearity of the ϕ plots. By varying the pressure of H_2, the exponent with respect to H_2 in the rate equation was found to be -1.2.

Iron

Neither of the methylhydrazines showed any deuterium exchange on iron. Decomposition of each compound occurred above ca. 290 K. For methylhydrazine there was an apparent activation energy of ca. 48 kJ mol^{-1} and the rate exponent with respect to H_2 was -1.0. For 1,1-dimethylhydrazine the apparent activation energy was ca. 44 kJ mol^{-1}.

Tungsten

No deuterium exchange of methylhydrazine on tungsten was observed. Decomposition of this compound occurred above ca. 370 K, producing methylamine and ammonia, with an apparent activation energy of ca. 33 kJ mol^{-1}, and an exponent of -1.1 with respect to H_2.

Deuterium exchange was observed with 1,1-dimethylhydrazine, but only at temperatures in excess of 390 K, and with only the d_1 compound being detected. This process had an apparent activation energy of ca. 19 kJ mol^{-1}. Decomposition, yielding ammonia and dimethylamine, was found to be significant only above ca. 470 K. This reaction was found to have an apparent activation energy of ca. 82 kJ mol^{-1} and an exponent of -0.4 with respect to the pressure of H_2.

DISCUSSION

In these experiments, the pattern of the deuterium exchange reactions occurring on palladium and platinum was as might have been anticipated, given the known (*1*) exchange behaviour of methylamine and dimethylamine on these metals. It appears that, here, the hydrazyl hydrogens behave very much as the amine hydrogens in the methylamines. The latter show similarities to those in ammonia, for whose exchange palladium and platinum serve as efficient catalysts (*14*). The behaviour is also similar to that of hydrazine itself on palladium (*5*).

The finding that the relative amounts of the various deutero-compounds satisfy the relevant equilibria is perhaps more notable in the case of methylhydrazine, where not all the hydrazyl hydrogen atoms are equivalent as are those of ammonia (*14*), but apparently all undergo exchange with equal ease.

There would appear to be two alternative explanations for the equilibrium among the exchanged products. One is that replacement occurs only one atom at a time, with exchange of only one H atom per visit of the molecule to the catalyst surface. In the case of methylhydrazine it needs also to be specified that all three hydrazyl hydrogens must exchange with equal ease. Kemball (*14*) has shown that such a process leads to the satisfaction of the equilibria:

$$d_0 + d_2 \rightleftharpoons 2d_1$$

$$d_1 + d_3 \rightleftharpoons 2d_2.$$

The other possibility is that, whether exchange may occur of more than one hydrogen atom at the time on the catalyst surface, interchange of H and D atoms may occur between two alkylhydrazine molecules on the acidic glass surface (*15*), either of the reaction vessel or of the glass capillary leak, so that when the alkylhydrazine molecules reach the mass spectrometer the above equilibria are satisfied. The present work does not enable these to be distinguished.

On nickel, there is no evidence that deuterium exchange of the methyl hydrogens occurs with either compound. Exchange occurs rather more reluctantly than on palladium and platinum, but it seems that only the hydrazyl hydrogens participate. This is in contrast to the behaviour (1) of methylamine and dimethylamine on this metal.

Whereas iron was found (1) to catalyse multiple exchange of methylamine and dimethylamine, it was apparently unable to catalyze exchange of these molecules. The reason would appear to be simply that these alkylhydrazines undergo decomposition on iron at temperatures below those at which deuterium exchange, presumably of the methyl hydrogens, might occur.

The behaviour of methylhydrazine on tungsten resembles that on iron. The significantly slower decomposition of 1,1-dimethylhydrazine permits its exchange on tungsten to be detected. Since only the d_1

compound was seen it is not possible to deduce which group of H atoms undergo reaction.

On all the metals employed, there is clear evidence that the decomposition of methylhydrazine is accompanied by the production of methylamine and ammonia and of 1,1-dimethylhydrazine by the production of dimethylamine and ammonia. The only occasion where any imbalance in the relative amounts of these products was suspected was on tungsten, where it is known (*9*) that ammonia readily forms a bulk nitride. Although, as explained in the Experimental section, hydrazine cannot be detected in the present system, it does seem clear that, in the catalytic decomposition, hydrogenolysis of the N–N bond predominates and the decomposition reaction will be considered on that basis.

A reliable measurement of the activation energy for decomposition requires at least two accurate rates at appreciably different temperatures. The behaviour of these alkylhydrazines in the mass spectrometer makes it difficult to achieve accuracy at a slow rate. The severe physical adsorption of the alkylhydrazines on glass, which leads to a strong memory effect (*1, 9*), upsets the accurate measurement of a fast rate. It is for these reasons that the figures quoted can only be approximate. However, it is clear that in all cases the activation energy for decomposition exceeds that for exchange.

In the exchange reaction on palladium, the exponents of D_2 pressure seem significantly different for the two alkylhydrazines. The value for methylhydrazine is fairly similar to that reported (*1*) for the exchange of methylamine on tungsten.

In most cases the decomposition reaction is found to be inhibited by hydrogen, which suggests that the catalyst surfaces are largely covered by hydrogen atoms. Catalytic dissociation of the N–N bond may well require the formation of a diadsorbed species, corresponding to that required (*8*) for C–N bond dissociation in alkylamines, and one must presume that the adsorbed hydrogen inhibits this step.

Only on tungsten is there any clear difference in the reactivity of the two compounds. It may be that of this metal both molecules undergo initial adsorption at a methyl group and that, by dissociative adsorption at both methyls, 1,1-dimethylhydrazine forms an α,γ-diadsorbed species, which might be expected to offer more resistance to the necessary rearrangement on the surface than would the singly adsorbed methylhydrazine, before N–N bond dissociation could occur.

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