

Catalytic Deuterium Exchange and Hydrogenolysis Reactions of 1,2-Dimethylhydrazine on Transition Metals

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It is shown that 1,2-dimethylhydrazine undergoes deuterium exchange of its hydrazyl hydrogens in the presence of D₂ and films of platinum, palladium, rhodium, nickel, or cobalt, but not iron or tungsten. Hydrogenolysis of the compound occurs on each of these metals, producing mostly methylamine, at slightly higher temperatures than the deuterium exchange, where the latter occurs. Various features of the exchange reaction over nickel suggest that it may not occur directly, but may involve catalytic deuterium exchange of the amine hydrogens of methylamine produced by hydrogenolysis, followed by an interchange of H and D between the amine and the hydrazyl hydrogens of 1,2-dimethylhydrazine, occurring on an acidic glass surface. The inability of iron and tungsten to catalyze deuterium exchange of 1,2-dimethylhydrazine could thus be correlated with their inability to catalyze exchange of the amine hydrogens of methylamine. © 1993 Academic Press, Inc.

INTRODUCTION

Earlier work (1) in this laboratory showed that exchange of the hydrazyl hydrogen atoms of methylhydrazine and 1,1-dimethylhydrazine occurred in the presence of deuterium at 273 K on palladium and platinum and above ca. 320 K on nickel. On tungsten, only 1,1-dimethylhydrazine underwent exchange and then only above ca. 390 K. Neither compound was found to undergo exchange on iron. On all those metals, both compounds were found to undergo hydrogenolysis at higher temperatures by rupture of the N-N bond. This reaction was accelerated by increasing temperature to a greater extent than was the exchange reaction.

These studies attested to the similarity of hydrazyl and amine hydrogen atoms in regard to catalytic deuterium exchange (2, 3) and to the facility with which the N-N bond may be ruptured on a transition metal catalyst.

The object of the present work is to extend these studies to 1,2-dimethylhydrazine (SDMH). It was thought that the behavior of this compound towards deuterium exchange

and hydrogenolysis would resemble that of methylhydrazine, with the slight but obvious difference that cleavage of the N-N bond would generate two identical product molecules. Earlier studies (4) of the thermal desorption products of the neat vapour of SDMH on the (111) face of a platinum single crystal showed that, under these conditions, methane, nitrogen, and dehydrogenation products were detectable.

EXPERIMENTAL

The apparatus, in glass with greased stopcocks, involved a demountable reaction vessel in which an evaporated film could be formed in high vacuum prior to the admission of the mixture of reactant gases, and from which a small amount (ca. 3% hr⁻¹) of the reacting mixture could be leaked away through a fine capillary to an MS10 mass spectrometer (5). Prior to deposition of the film, the reaction vessel was baked at 350°C for 2 h and the filament was outgassed for 0.5 h. Then, with the reaction vessel immersed in ice water, evaporation was performed over 10-15 min, producing a film of ca. 10 mg (5, 6). The premixed gases were

then expanded into the reaction vessel while the film was at 0°C. In this way a reproducible surface of the chosen transition metal could be generated to act as a catalyst.

To prepare SDMH, Aldrich 99% grade 1,2-dimethylhydrazine dihydrochloride was dropped, in an evacuated part of a vacuum line, on to powdered KOH. The vapour given off when this mixture was heated was condensed into an evacuated tube containing barium oxide powder to remove water vapour (7). Reaction mixtures were made up using the vapour along with 99.5% pure hydrogen or deuterium. The methylamine used for calibration of the mass spectrometer and for special experiments was of Matheson reagent grade and was thoroughly degassed after being admitted to the vacuum line.

The mass spectrometer peaks from SDMH showed good correspondence with those listed by Dibeler et al. (8). It was found convenient to work with an electron accelerating voltage of 15 V, at which the parent peak was a little larger than the $m/z = 45$ peak, attributable (8) to the ion $\text{CH}_3\text{N}_2\text{H}_2^+$. Since there was a negligible yield, with 15 eV electrons, of ions of $m/z = 59, 58, 44,$ and 43 , no fragmentation corrections needed to be applied to ions of mass number greater than 60 and 45 in order to evaluate the extent of deuterium exchange. From the amounts d_i of the molecule with i atoms of deuterium a parameter ϕ was calculated from the following equation:

$$\phi = \frac{\sum_{i=1}^n (id_i)}{\sum_{i=0}^n (d_i)} \quad (1)$$

On all metals where deuterium exchange was observed, it was found that a maximum of two D atoms could be incorporated per molecule. Very similar ϕ values were obtained using, on the one hand, the peaks 60, 61, and 62 and, on the other, the peaks 45, 46, and 47. This combined with the assignment (8) of the $m/z = 45$ peak of SDMH to

the fragment ion $\text{CH}_3\text{N}_2\text{H}_2^+$ confirmed that the observed exchange was exclusively of the hydrazyl hydrogens, and did not involve the methyl hydrogens. Also, at all times the ratio d_1^2/d_0d_2 was, within experimental error, equal to 4, which is the value to be expected where these three species are in equilibrium (9).

Plots of $\ln(\phi_x - \phi)$ against time (t) were used to obtain the pseudo-first-order rate constant for deuterium exchange, where ϕ_x was calculated (2) as $P_{\text{D}_2}/(P_{\text{D}_2} + P_{\text{SDMH}})$ on the premise that only the hydrazyl hydrogens were available for exchange. Mostly these plots were found to be linear except where substantial decomposition of SDMH occurred and where the deuterium pressure was not much greater than that of SDMH. Under these conditions the ϕ_x value ceases to be a constant and must change appreciably as decomposition occurs, since this sharply alters the ratio of the amount of D_2 to that of the hydrogen atoms, on amine and hydrazyl groups, which can undergo exchange with it.

RESULTS

Nickel

When a mixture of SDMH vapour and D_2 was admitted to a fresh nickel film at 273 K, no deuterium exchange was detectable. On raising the temperature to ca. 320 K, exchange was observed at a rate which increased over 20–40 min similarly to the acceleration shown in Fig. 1. When the temperature was raised again to ca. 370 K, faster exchange was found but at a steady rate. The pseudo-first-order rate constants before ($3.0 \times 10^{-3} \text{ min}^{-1}$) and after ($4.5 \times 10^{-3} \text{ min}^{-1}$) this second temperature increase show an acceleration by a factor of 1.09 per 10 K rise in temperature.

However, within this temperature range, SDMH also undergoes an N–N bond fission reaction, producing methylamine. This was not observed at 273 K, but was in evidence at and above 320 K. A notable feature of this decomposition, in the presence of D_2 ,

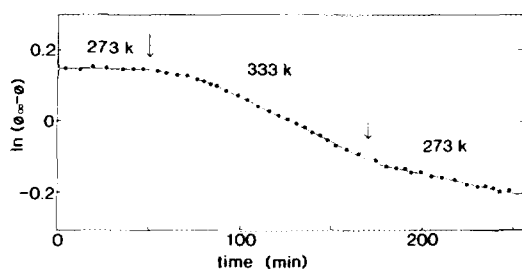
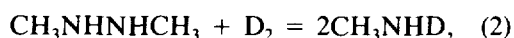


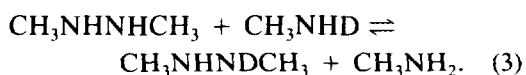
FIG. 1. Plot of $\ln(\phi_x - \phi)$ against time for an experiment on a nickel film, where initially there was no exchange of 1,2-dimethylhydrazine at 273 K but where exchange occurred at this temperature at the expected rate after the film had been held for a time at 333 K.

was that although one might write the equation for the reaction as



the initial yield of methylamine was almost entirely the d_0 isomer, CH_3NH_2 .

The simplest rationalisation of this observation requires that isotopic equilibria exist, not merely among the various deuterated SDM_H species and among the various deuterated methylamine species, but also between these two groups, viz.,



This would require that the extent of deuterium exchange of the product methylamine should increase in parallel with that of SDM_H, which was indeed found to be the case.

In the light of the above, the increase with time in the rate of exchange at 320 K suggests that this acceleration may be closely related to the extent of SDM_H hydrogenolysis to methylamine. To test this hypothesis, two further experiments were carried out. In the first, after the admission of the usual gas mixture to the nickel catalyst at 273 K, no reaction was observed. When the temperature was raised to 333 K, deuterium exchange occurred at a rate which increased over ca. 35 min, as shown in Fig. 1. By this time, ca 5% of the SDM_H had undergone

hydrogenolysis to methylamine. Thereafter the plot of $\ln(\phi_x - \phi)$ against time remained linear. The reaction vessel was then cooled down again to 273 K, with the consequence that deuterium exchange continued, but at a slower rate. From the slopes of the plots of $\ln(\phi_x - \phi)$ before and after this temperature change, the acceleration with temperature rise was evaluated as a factor of 1.10 per 10 K, in acceptable agreement with the value from the earlier experiment.

Thus it would appear that no deuterium exchange of SDM_H may be seen on nickel except when some methylamine is present. The observed acceleration of the exchange at 320 K coincides with the increasing amount of methylamine present on account of the hydrogenolysis process. At 273 K in the absence of methylamine no deuterium exchange of SDM_H was seen; however, after a period of time at 333 K had caused some decomposition of SDM_H, exchange occurred at 273 K at the rate to be expected from the back extrapolation using the rate constants for exchange at higher temperatures. It thus appeared that methylamine has a clear role in the deuterium exchange of SDM_H.

In the other experiment, in making up the reaction mixture a small amount of methylamine was added, equal to 15% of the partial pressure of SDM_H. When this was admitted to a fresh nickel film at 273 K, no deuterium exchange of SDM_H was seen over 2 h. When the temperature of the catalyst was raised to 330 K, deuterium exchange occurred after a much shorter induction period than in the previous experiment. When the catalyst was cooled again to 273 K, the deuterium exchange continued but at a slightly slower rate.

From this experiment it is clear that the presence of methylamine is not sufficient to enable deuterium exchange of SDM_H to occur at 273 K. From one aspect this is not surprising since the temperature range quoted (2) for the study of deuterium exchange of methylamine on this metal

(304–453 K) does not include the value in question.

Decomposition of SDMH, in the presence of either H₂ or D₂, was found to follow first order kinetics. The difficulties experienced in the earlier studies (1) continued to affect the measured rates of very slow or very fast reactions but the activation energy for hydrogenolysis on nickel was found to be ca. 56 kJ mol⁻¹. The main product was methylamine, but dimethylamine and trimethylamine were also in evidence, particularly at the higher temperatures. By carrying out successive experiments on the same film with different H₂ pressures it was found that the rate exponent with respect to H₂ was -0.6, indicating inhibition by adsorbed hydrogen.

Iron and Tungsten

No deuterium exchange was observed over films of either of these metals, even at temperatures where rapid decomposition was occurring. On both metals, the decomposition products included dimethylamine and trimethylamine.

Over iron, the apparent activation energy for decomposition was ca. 50 kJ mol⁻¹, and increased hydrogen pressure caused a slight decrease in the rate, with a formal kinetic order of -0.2. On tungsten films, the corresponding figures were found to be ca. 68 kJ mol⁻¹ and +0.7, the latter indicating that adsorbed hydrogen assisted the reaction.

To interpret the difference in regard to deuterium exchange of SDMH, it is instructive to recall that whereas the amine hydrogens of methylamine were found (2) to undergo exchange over nickel, it was the methyl hydrogens which most readily underwent exchange over tungsten and iron.

Over iron, and to a much lesser extent on tungsten, as SDMH decomposed in the presence of D₂, a methylamine isotope peak was seen to grow at *m/z* = 32, consistent with the exchange of a methyl hydrogen of methylamine. The rate was rather less than would have been deduced from the previous studies (2), but one may presume that deute-

rium exchange is inhibited by the adsorbed species present on the surface while SDMH decomposition is occurring. However, just as no H/D exchange occurs among isotopically substituted methanes (15) or between the methyl and the amine hydrogens of methylamine (2), no interchange of D atoms is to be expected between CH₂DNH₂ and either type of hydrogen atom in SDMH.

Cobalt

Over films of cobalt, scarcely any deuterium exchange of SDMH could be observed below ca. 350 K. At 378 K, exchange was seen at a rate which increased with time, and faster exchange was observed at higher temperatures.

On cobalt, the hydrogenolysis reaction was clearly in evidence above 378 K, and from the rates at higher temperatures the activation energy was evaluated as ca. 55 kJ mol⁻¹. Thus the behaviour on cobalt is in many respects intermediate between that found on nickel and on iron.

Platinum

When a mixture of SDMH vapour and D₂ was admitted to a fresh platinum film at 273 K, deuterium exchange of up to two H atoms, clearly the hydrazyl hydrogens, was seen at once. Since the kinetics of an individual exchange run, in which it is only the isotopic composition and not the concentration which varies, tells nothing of the true reaction order (10), a set of experiments was performed in which the pressure of D₂ was varied while that of SDMH was kept constant. The slopes of the ϕ plots at 273 K were used to evaluate the order of the exchange reaction with respect to D₂. The relevant equation has been shown (10) to be

$$\ln\left(\frac{\phi_{\infty}}{\phi_{\infty} - \phi}\right) = \frac{k_n(P_{D_2} + P_{SDMH})t}{(P_{D_2})^{1-p}(P_{SDMH})^{1-q}}$$

where *p* and *q* denote the orders of reaction with respect to D₂ and SDMH. Thus the pseudo-first-order rate constant derived from a ϕ plot is really equal to $k_n(P_{D_2} + P_{SDMH})(P_{D_2})^{p-1}(P_{SDMH})^{q-1}$.

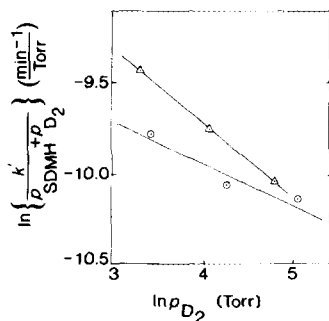


FIG. 2. Plot of $\ln\{k'/(P_{\text{SDMH}} + P_{\text{D}_2})\}$ against $\ln P_{\text{D}_2}$ for the exchange of 1,2-dimethylhydrazine with a variable pressure of D_2 at 273 K over films of (○) platinum and (△) palladium.

From the plot of $\ln\{k'/(P_{\text{SDMH}} + P_{\text{D}_2})\}$ against $\ln P_{\text{D}_2}$ shown in Fig. 2, where k' denotes the pseudo-first-order rate constant for exchange, adjusted to a film of 10 mg weight, the order with respect to deuterium of the exchange reaction on platinum was found to be ca. +0.8.

At 273 K, the SDM_H also undergoes N–N bond fission. At this and higher temperatures, the only product seen was methylamine, with no dimethylamine or trimethylamine. The activation energy was found to be ca. 55 kJ mol⁻¹ and the order of the hydrogenolysis reaction with respect to hydrogen was ca. +0.6.

Thus on this metal also, the deuterium exchange and hydrogenolysis reactions are closely associated. However, at those lower temperatures where one would estimate that the rate of the latter could be neglected, the vapour pressure of SMDM would be so low that no studies of the present type would be possible. Thus it is not feasible on platinum to look for deuterium exchange of SDM_H at temperatures where the rate of hydrogenolysis is negligible.

Palladium

On palladium, also, immediate deuterium exchange of the hydrazyl hydrogens was observed at 273 K. From a set of experiments in which the deuterium pressure was varied,

the reaction order with respect to D_2 was found to be +0.6, as shown in Fig. 2.

Some hydrogenolysis to methylamine was evident even at 273 K. By varying the H_2 pressure, the exponent for H_2 in the rate equation was found to be -0.6. On this metal, dimethylamine and trimethylamine were among the products and seemed to be formed under conditions where negligible decomposition of methylamine, the main product, was occurring.

Rhodium

Over a rhodium film, the rate of exchange increased for ca. 20 min. after the reaction mixture was admitted at 273 K, and then remained constant. Thus the behaviour resembles that exhibited on nickel and cobalt.

Very slow hydrogenolysis of SDM_H was observed at 273 K. From the rates at higher temperatures the activation energy was evaluated as 42 kJ mol⁻¹.

Methylamine and SDM_H

Since the pattern of the deuterium exchange results led to the postulate that, at least on some metals, methylamine resulting from SDM_H decomposition was involved, it was considered desirable to demonstrate that the H/D interchange described in Eq. (3) would actually take place.

A mixture of methylamine and D_2 was admitted to a freshly prepared palladium film and the exchange reaction was seen to occur in the expected manner (2). When this reaction had produced substantial amounts of MeNHD and MeND₂, the mixture was pumped out via a trap at 77 K, to collect the methylamines. Amounts of SDM_H and H_2 were added to the latter and the mixture, without any contact with the palladium catalyst, was again allowed to leak into the mass spectrometer. It was found, right from the first scan, both from the $m/z = 60$ parent peak and from the $m/z = 45$ fragment peak, that there had been substantial deuterium exchange of the SDM_H, to yield the d_1 and d_2 products. Clearly, the origin of these can only have been the MeNHD and MeND₂

produced in the earlier catalytic process so that reaction (3) must take place quite freely on the glass surface.

DISCUSSION

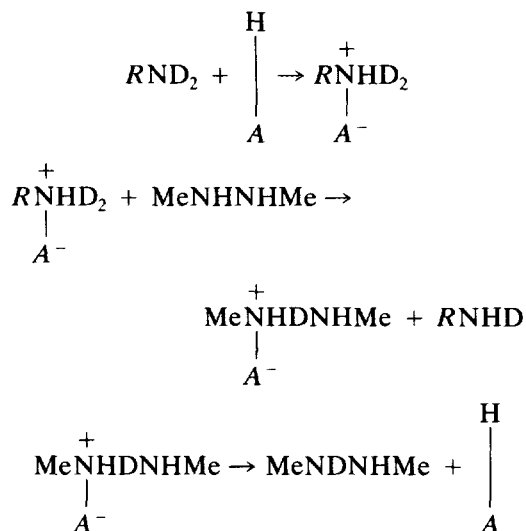
The occurrence of deuterium exchange of 1,2-dimethylhydrazine on transition metals appeared to be closely linked to the decomposition of this molecule to methylamine. However, while no deuterium exchange was detected except where some methylamine was present, the extensive studies on nickel films showed that the presence of methylamine, while it may seem to be essential, is not sufficient to enable deuterium exchange to occur at 273 K. Since in the experiment with a small amount of methylamine added to the SDMH, it was necessary to initiate the reaction at a higher temperature before exchange could be detected at 273 K, it is likely that some conditioning of the surface must occur before the exchange reaction becomes possible.

The fact that no exchange of SDMH was detected except when some methylamine was present suggests the possibility that the mechanism involves first the exchange of D₂ with methylamine (2) to form CH₃NHD and CH₃ND₂, followed by the interchange of H and D between the amine hydrogens of methylamine and the hydrazyl hydrogens of SDMH. The auxiliary experiments in the present work show that this latter process occurs very rapidly, so that the rate of formation of deuterated SDMH would be determined by the first step.

However, this is not necessarily the case. The occurrence of some N-N bond homolysis before deuterium exchange is detectable may simply reflect the vulnerability of this middle bond of SDMH on these transition metals, to the extent that some methylamine will be formed before deuterium exchange is observable. In that event, the presence of methylamine when deuterated SDMH is detected would be a concomitant event rather than the necessary cause.

In either case, it is clear that ready interchange of H and D must occur between

MeND₂ and SDMH. The mechanism is most probably analogous to that for the scrambling of H and D atoms among the d₀- to d₃-ammonias (11) and involves the adsorption of the alkylamine and SDMH molecules at acidic centres on the glass surface, written for short as HA. A reaction sequence may be postulated as follows:



These steps add up to the reaction



The above mechanism assumes that the acidic centres on the glass surface act as Brønsted rather than Lewis acids. In the present work it was noted that when a sample of methylamine that had been substantially exchanged with deuterium was condensed in a trap containing glass wool, on returning it to the vessel connected by the capillary leak to the mass spectrometer, the D content had decreased very considerably, as if the glass wool had reversed the deuterium exchange. This finding would suggest the abundant presence of Brønsted acid sites on the glass surface.

The issue does arise of why SDMH would not undergo direct deuterium exchange on the surface of metals such as cobalt, iron, and tungsten. On the face of it, there would seem to be no overpowering difficulty. The

answer must be that although the molecule can readily adsorb on the metal surface, it has difficulty in desorbing as 1,2-dimethylhydrazine. That is, it tends to dissociate before coming off. These metals are all quite efficient as catalysts for ammonia synthesis and all have "a high affinity for nitrogen" (14) as evidenced by their formation of bulk nitrides (15). Of the other metals, platinum and palladium have much lower "affinity for nitrogen" and desorption of the undissociated molecule may conceivably be feasible. In this connection it is notable that the formal orders of the exchange reaction with respect to D_2 on these metals are quite similar and are close to the value found for the deuterium exchange of methylhydrazine on palladium. Such values appear consistent with Langmuir-Hinshelwood kinetics and a formal dependence of the reaction rate between $P_{D_2}^{1/2}$ and P_{D_2} .

In the light of the present work, one must wonder whether any contribution from a comparable indirect mechanism is involved in the deuterium exchange of methylhydrazine and 1,1-dimethylhydrazine, studied previously (1). One difference is that the hydrogenolysis of these compounds produces an alkylamine and ammonia, either of which could participate in deuterium uptake. In that work (1), it was not suspected that hydrogenolysis products must be present if deuterium exchange were to take place. However, a comparison of the results shows that, except on Fe, hydrogenolysis of SDMH tends to occur at slightly lower temperatures than did that of the alkylhydrazines studied previously (1). This effect may be attributable to having a methyl group attached to each N-atom.

However, the close similarity of the conditions for observing, on each metal except iron, deuterium exchange and hydrogenolysis of either methylhydrazine or 1,1-dimethylhydrazine (1) admits of the clear possibility that the same mechanism is applicable, with deuterium transfer to the alkylhydrazine at least from the alkylamine if not also from ammonia. An exception

seems necessary in regard to the small amount of exchange of 1,1-dimethylhydrazine on tungsten (1), which is probably replacement by D of one of the methyl hydrogens, occurring just like the corresponding reaction (2) of dimethylamine.

An interesting feature of the present work is that under conditions where SDMH undergoes hydrogenolysis, on certain metals the products include dimethylamine (DM) and also triethylamine (TM). This finding is redolent of the identity of the products of $MeNH_2$ and $EtNH_2$ hydrogenolysis on these metals (16, 17), in that Kemball and Moss (17) observed very little diethylamine and triethylamine on platinum but appreciable amounts on palladium and nickel.

However, one slight difference is that in the present work it is not apparent that the formation of DM and TM can totally be correlated with the decomposition of $MeNH_2$. On palladium in particular, the yields of DM and TM were seen to rise while that of $MeNH_2$ was essentially stationary. This suggests that the products DM and TM may be generated from the adsorbed residues of NHMe formed by N-N bond fission of SDMH, and is consistent with the discussion (16) of the hydrogenolysis of $MeNH_2$ in terms of the C_1N_1 , C_2N_1 , and C_3N_1 skeletal units.

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