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Methane-Deuterium Exchange over Platinum-Rhodium Alloys

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The rate of exchange between methane and deuterium has been studied on a series of unsupported platinum-rhodium alloys in the temperature range 80° to 150°. Stepwise exchange, leading to the successive formation of deuteromethanes, was the most important mechanism on all the alloy samples at the lower temperatures. The initial rates of formation of the species CHD_3 and CD_4 arising from multiple exchange increased with increasing temperature. The specific activity of the alloys reached a maximum at a composition of 60–70 wt % rhodium, corresponding to one unpaired *d* electron per metal atom. Factors which may influence the mechanism of exchange on the platinum group metals are discussed.

INTRODUCTION

The rate of the exchange reaction between methane and deuterium has recently been used to investigate patterns of catalytic activity in binary alloys of the noble metals (*1*, *2*). Although details of the mechanism remain obscure, this reaction appears to have advantages of simplicity over more widely used reactions, such as formic acid decomposition or ethylene hydrogenation, in which the kinetics are often complicated by competing side reactions and retardation by products.

Earlier work by Kemball (*3*) on methane–deuterium exchange over evaporated films, indicated that metals of the platinum group vary with respect to their ability to promote either stepwise exchange, with the successive formation of deuterated methanes from CH_4, or multiple exchange, with the initial formation of highly deuterated species. Previous work in this series (*1*) suggested that two noble metals, such as platinum and ruthenium, which in the pure state exhibit different types of exchange mechanism, will show only stepwise exchange under the same conditions when combined into binary alloys. The contribution of multiple exchange does, however, tend to increase with increasing temperature; furthermore the specific activity of alloys for this exchange reaction is often not a simple linear function of alloy composition. Thus the Pt-Ru system shows a maximum in activity at around 10–25 wt % Ru at 90°, whereas no such effect was observed for alloys of Pt-Pd and Pd-Rh (*2*).

In a further application of this method, the exchange reaction over platinum-rhodium alloys has been studied. In the pure state these metals show comparable activity at about 100°, although rhodium has a greater tendency to exhibit multiple exchange than does platinum under the same conditions.

EXPERIMENTAL

The methods of preparing the powdered alloy samples and experimental techniques used in the exchange experiments have been adequately described in previous publications (*1*, *2*) and only a brief summary will be given here.

The alloys were prepared by co-reduction of mixed solutions of chloroplatinic acid and rhodium trichloride with 5% sodium borohydride solution. The coagulated products were washed thoroughly, dried in air, then reduced in flowing hydrogen for 3 hr at 300°, after first flushing with a stream of nitrogen at room temperature. The products were black powders with BET surface areas in the range 4–5 m^2/g. When the initial nitrogen flushing step was omitted, in two cases the catalyst became momentarily pyrophoric during the reduction treatment and the resulting surface areas were reduced to 3 m^2/g. These latter samples were gray and somewhat granular in appearance and showed a lower specific activity than the other alloys used in this work. The observed pyrophoricity probably arises as a result of the catalyzed reaction between hydrogen and oxygen entrained in the samples. Even in the absence of air, for example after flushing with nitrogen or after evacuation, some sintering of the alloys occurs on contact with hydrogen, presumably on liberation of the heat of reduction of chemisorbed oxygen.

The exchange experiments were carried out on 1-g samples of the reduced alloys, which had previously been evacuated to 1×10^{-6} mm and then saturated with deuterium. Forty millimeters of deuterium were then admitted to the sample cell (dead volume = 16 ml) followed by 80 mm of methane and the progress of the exchange reaction was determined by means of a mass spectrometer connected directly to the sample cell. It was found at an early stage in this work that the alloy samples were rapidly poisoned by mercury vapor present in the apparatus. For this reason gold foil traps were used throughout to protect the metals from contamination. These traps were replaced frequently but cooling to below room temperature was found to be unnecessary.

An ionizing voltage of 70 V was used in the mass spectrometer and the concentration of the deuteromethanes was calculated directly from the fragmentation patterns of pure samples of the products determined over a range of pressure. A complete analysis of mass peaks 12 to 20 could be made in under 2 min. The catalytic activity of the samples could always be completely restored by treatment with deuterium at 150° for a few minutes at the end of each measurement. Exchange experiments were carried out on each alloy sample at several different temperatures in the range 80° to 150°.

The homogeneity and lattice parameters of the alloys were determined from Debye-Scherrer X-ray diffraction patterns. All the preparations in this alloy series were found to be homogeneous solid solutions with lattice spacings which agreed well with the literature values. The compositions of the alloys were determined by X-ray emission spectroscopy.

RESULTS

In order to calculate the rate constants of the exchange reactions from the observed rates of formation of the deuteromethanes, the first order equations given by Kemball (*4*) were used.

The initial rate of substitution of deuterium atoms into 100 molecules of methane in unit time, k_ϕ, is given by the expression

$$-\log_{10}(\phi_\infty - \phi) = (k_\phi t/2.303\phi_\infty) - \log_{10}\phi_\infty \quad (1)$$

where ϕ is defined by

$$\phi = \sum_{i=1}^{4} i x_i$$

x_i being the percentage of the species containing i deuterium atoms present at time t and ϕ_∞ is the equilibrium value of ϕ.

The initial rate of disappearance of light methane CH_4, in percentage per unit time, k, was calculated from the equation

$$-\log_{10}(X - X_\infty) = [kt/2.303(100 - X_\infty)] - \log_{10}(100 - X_\infty) \quad (2)$$

where X and X_∞ are the percentages of CH_4 present at time t and at equilibrium, respectively.

The mean number of hydrogen atoms being replaced initially in each molecule of methane is given by the ratio

$$M = k_\phi/k$$

Equations (1) and (2) were found to fit the exchange data quite well in the initial stages of reaction, enabling values of k_ϕ, k, and M to be determined from each experiment. Deviations from these first order equations began to appear as appreciable quantities of the deuteromethanes accumulated in the gas phase. By assuming a binomial distribution of species at each stage, it is possible to predict the course of the exchange reaction over a more extended period, as shown recently by Mikovsky and Wei (*5*). However, in the present work only the initial rates of exchange were of interest and the simplified equations above were found to be adequate.

All of the alloy samples of the Pt-Rh system were quite active in the exchange reaction over the temperature range studied, the time required for the disappearance of half the CH_4 present ranging from 5 to 40 min at about 100°. As found previously (*2*), both metals in the pure state show similar specific activity at temperatures around 100°, with platinum becoming relatively more active than rhodium with increasing temperature. This result is not in agreement with the data presented by Kemball (*3*), who found that rhodium was more active than platinum at 200° over evaporated metal films. The reason for this discrepancy is not known.

In the present work rhodium exhibited a somewhat greater tendency than platinum to promote multiple exchange and all the Pt-Rh alloys showed mainly stepwise exchange, with increasing contributions from multiple exchange at the higher temperatures. A typical set of results is shown in Fig. 1, representing the hydrocarbon com-

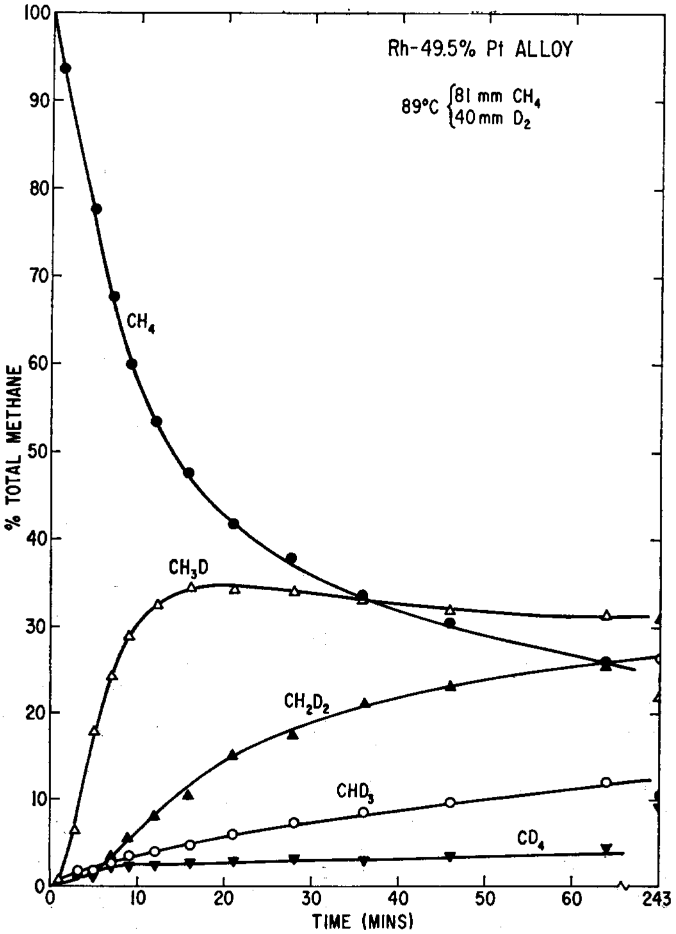


FIG. 1. CH_4–D_2 exchange on Rh-49.5% Pt alloy, 89°C.

position of the gas phase as a function of time. In this case the initial rates of formation of the deuteromethanes decreased regularly with deuterium content. An illustration of multiple exchange behavior is shown in Fig. 2 for another alloy sample at a higher temperature. In this experiment the initial rates of formation of CHD_3 and CD_4 were much much greater than that of CH_3D. As in previous work, the initial rate of the stepwise process, R_1, could be estimated from the initial rate of CH_3D formation and that for multiple exchange, R_2, from a plot of $(CH_2D_2 + CHD_3 + CD_4)$ as a function of time. The average number of H atoms being exchanged by D, or the exchange number M, could also be found as described above.

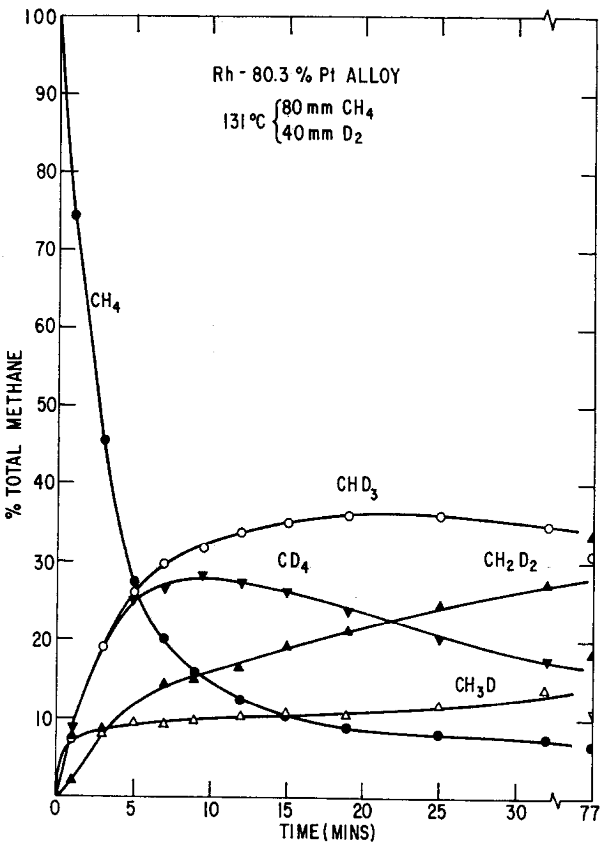


FIG. 2. CH_4-D_2 exchange on Rh-80.3% Pt alloy, 131°C.

Table 1 is a compilation of the exchange data obtained for the Pt-Rh series. Columns 1 and 2 give the composition and lattice spacings, a_0, of the samples. The surface areas, as determined by the BET method using nitrogen adsorption at −196°, are recorded in column 3. The temperature of the exchange runs is given in column 4 and the time, $t_{1/2}$, required for half the original CH_4 to disappear in column 5. Columns 6 and 7 show the values of the first order rate constants k_ϕ and k, calculated from Eqs. (1) and (2) above and expressed in molecules/sec/cm^2 of metal surface. The mean initial exchange number M and the ratio of the rates of stepwise to multiple exchange, R_1/R_2, are shown in columns 8 and 9. The last two alloy samples in this table ignited spontaneously on reduction with hydrogen. These showed lower surface areas and reduced catalytic activity owing to more extensive sintering.

TABLE 1
METHANE-DEUTERIUM OVER PLATINUM-RHODIUM ALLOYS[a]

Catalyst comp. (wt %)	Lattice const, a_0 (Å)	Surface area (m^2/g)	Temp (°C)	$t_{1/2}$ (min)	Molecules/sec cm^2		M	R_1/R_2
					$k\phi$	k		
100 Pt	3.916	4.9	83	—	1.33×10^{11}	1.02×10^{11}	1.3	6.1
			139	1	8.3×10^{12}	4.91×10^{12}	1.7	1.9
80.3 Pt	3.896	4.3	96	10.5	1.1×10^{12}	1.08×10^{12}	1.0	2.0
			110	6.3	2.7×10^{12}	1.59×10^{12}	1.6	1.2
			131	2.5	1.25×10^{13}	3.08×10^{12}	4.0	0.2
49.5 Pt	3.849	4.5	89	14.0	1.55×10^{12}	9.35×10^{11}	1.2	3.9
			110	3.3	3.88×10^{12}	2.08×10^{12}	1.9	0.9
14.7 Pt	3.816	4.9	74	—	2.4×10^{10}	2.32×10^{10}	1.0	10.0
			96	51	3.72×10^{11}	3.39×10^{11}	1.1	4.5
			113	8.0	1.64×10^{12}	1.16×10^{12}	1.4	1.9
100 Rh	3.804	4.4	99	46	3.2×10^{11}	3.19×10^{11}	1.0	3.9
			127	6.0	1.51×10^{12}	8.85×10^{11}	1.7	1.1
			137	4.3	2.90×10^{12}	1.16×10^{12}	2.5	0.7
61 Pt	3.859	3.0	108	40	8.39×10^{11}	6.60×10^{11}	1.3	4.6
			128	5.3	3.23×10^{12}	2.40×10^{12}	1.4	1.4
			132	3.5	6.98×10^{12}	3.90×10^{12}	1.8	0.8
67.8 Pt	3.863	3.0	91	110	2.0×10^{11}	2.12×10^{11}	1.0	7.5
			107	15.7	1.3×10^{12}	1.26×10^{12}	1.0	4.0
			122	6.3	3.3×10^{12}	2.07×10^{12}	1.6	1.3

[a] 1 g alloy samples. 80 mm CH_4 + 40 mm D_2 initially.

As noted before for other alloy series, there is a general tendency for the contribution of multiple exchange to increase with increasing temperature. Evidence for this is found in the increasing values of M and decreasing values of R_1/R_2 found for all samples with increasing temperature. In every case, however, almost complete stepwise exchange was observed below 100°.

The activation energies for the exchange process did not show any regular variation with alloy composition and owing to the limited range of temperature employed with each sample, these kinetic parameters could not be determined with high precision. Values for the activation energy for stepwise exchange ranged from 6 to 20 kcal/mole; for multiple exchange from 16 to 34 kcal/mole; and for the initial disappearance of CH_4, from 10 to 23 kcal/mole. In every case the activation energy for the multiple exchange process considerably exceeded that for stepwise exchange—a result which has been confirmed with every alloy system studied so far.

By using the derived kinetic parameters, the specific rate of the exchange reaction could be compared for all the alloy samples at a particular reference temperature. Figure 3 shows the changes in the values of the rate constant for the initial disappearance of CH_4, k, and the corresponding rates of the two processes R_1 and R_2 as functions of alloy composition at 100°. Only the first five samples in Table 1 are included and the rates are expressed in molecules/sec cm^2 to eliminate small differences in the surface areas of the catalysts. Although the values of k for the two pure metals are similar at this temperature, a pronounced maximum in all three parameters was found for alloys containing between 60 and 70 wt % platinum. At this point the over-all rate of exchange was about 3.5 times faster than over pure platinum. A similar maximum in specific activity was found in the Pt-Ru system (*1*), but not for Pt-Pd or Pd-Rh alloys (*2*).

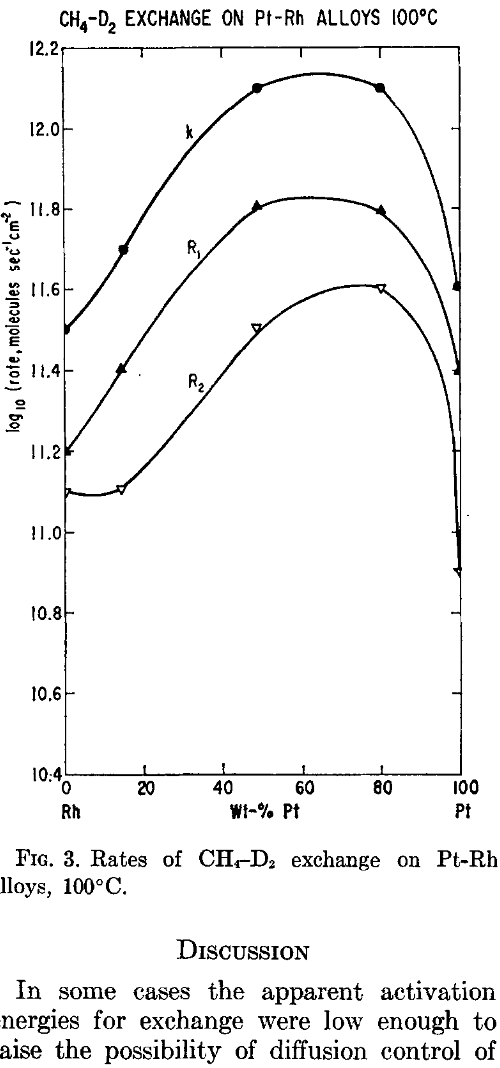


FIG. 3. Rates of CH_4–D_2 exchange on Pt-Rh alloys, 100°C.

DISCUSSION

In some cases the apparent activation energies for exchange were low enough to raise the possibility of diffusion control of the kinetics. In order to estimate the importance of this effect, calculations were made of the approximate diffusion coefficient and of the fraction of the available surface being utilized in the reaction according to the method developed by Wheeler (*6*). With a gas pressure of 0.1 atm and an average pore size of approximately 100 Å, diffusion would be of the Knudsen type in the temperature range considered. The diffusion coefficient would then be of the order of 0.1 cm²/sec.

For a static system, the fraction of surface available is

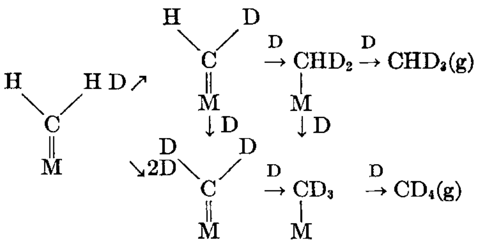
$$f = (1/h) \tanh h$$

where the parameter $h \tanh h$ is defined by

$$h \tanh h = a^2 0.693 V_R / 18 D t_{1/2} V_g W$$

a being the diffusion path length, $t_{1/2}$ the time in seconds for the completion of 50% reaction in a reactor of dead volume V_R, containing W grams of catalyst of pore volume V_g. For a typical experiment at 130°, taking $t_{1/2} = 120$ sec, and assuming a diffusion path length of 3 mm, the fraction of surface available is approximately 0.997. Thus even at the highest temperatures used it is unlikely that diffusion plays a significant role in determining the kinetics of the exchange reaction.

Many details of the mechanism of exchange reactions on metals need further elucidation. For example, the reason for the greater tendency of rhodium than platinum to exhibit multiple exchange still remains somewhat obscure. As observed previously (*2*), Pt and Pd give rise to substantially less multiple exchange under the same conditions than do Rh, Ru, and Ir. Although it has been argued (*4*) that multiple exchange involves extensive dissociation of chemisorbed methane to methine radicals CH, or even to carbon atoms on the metal surface, it seems more likely that dissociation does not proceed beyond the methylene stage CH_2. The highly deuterated products characteristic of multiple exchange could then arise as a result of a rapid exchange of the hydrogens of the CH_2 radical by surface deuterium atoms, followed by deuteration of the metal–carbon double bond and subsequent desorption of the saturated species. The adsorbed methylene radical can be imagined to pass through a succession of isotopic changes on progressive deuteration



In support of this idea there is some experimental evidence that unsaturated hydrocarbon species often undergo exchange more readily than addition at elevated temperatures. Thus Turkevich, Schissler, and Irsa (*7*) found that exchange of ethylene with deuterium was more rapid than deuteration over a nickel wire at 90°. As the concentration of hydrogen atoms on the metal surface is certainly low during the course of the exchange reaction, owing to the excess D present and to the very rapid rate of the H + D exchange reaction, the probability that these hydrocarbon intermediates will pick up H rather than D is slight.

It seems likely that the ability to promote multiple exchange is related to the stability of complexes of the type H_2C=Metal. By analogy with the stability of olefin–metal compounds (*8*), it might be expected that the methylene radical will bond more strongly to a Pt or Pd atom than to Rh or Ru, although actual complexes of this type do not appear to have been isolated. A strong bond of this nature might inhibit the deuteration of the C=Metal bond and thus suppress the multiple exchange process. Assuming an inverse relation between the ability to promote multiple exchange and the strength of the C=Metal bond, it might be expected that the occurrence of multiple exchange would increase in the order $\mathrm{Pt} \leq \mathrm{Pd} < \mathrm{Rh} < \mathrm{Ru} \approx \mathrm{Ir}$. Such a sequence was indeed found for the CH_4–D_2 exchange reaction (*2*) and by Addy and Bond for propane–D_2 exchange over pumice-supported noble metals (*9*).

Expressed differently, the formation of multiply bonded radicals may be related to the concentration of electron vacancies in the *d* band of the metal, according to the electronic picture of catalysis developed by Dowden (*10*). In this connection studies of catalytic patterns in alloy systems are useful in assessing the relative importance of geometrical and electronic factors in determining catalytic activity. Thus in the present case, assuming the surface structure of the alloys to be identical with that of the bulk, the variation in specific activity of the alloys shown in Fig. 3 cannot be explained in terms of the lattice parameters of the samples as these change approximately linearly with alloy composition according to Vegard's law (*11*), and in any case, the variation of lattice spacing in the series is very small. It seems more likely that the electronic configuration of the alloys is of deciding importance in this case.

Rhodium has nine electrons ($4d^85s$ in the ground state) outside a Kr core, whereas platinum has 10 outer electrons. This amounts to approximately 1.4 unpaired *d* electrons per atom for Rh, compared with 0.6 for Pt (*12*). Thus, assuming a linear variation in electronic properties throughout the alloy series, a concentration of one unpaired electron per atom corresponds to an alloy composition of 65.5 wt % Pt, in close agreement with the maximum in catalytic activity shown in Fig. 3. Recent work on *n*-pentane isomerization on supported alloy catalysts by Gray, Masse, and Oswin (*13*) supports the idea that optimum catalytic activity is often associated with an unpaired electron concentration of one per metal atom. Nishimura (*14*) has recently reported a maximum in the activity of Pt-Rh alloys for the hydrogenation of aromatic molecules, although in this case the optimum composition occurred at 60–90% Rh. The previously reported maximum in the exchange activity of Pt-Ru alloys can be accounted for on the same basis. Ru has 2.2 unpaired *d* electrons per atom, leading to one electron absence in the *d* band at 15 wt % Ru, a composition which agrees closely with the observed activity maximum for the exchange reaction (*1*).

Unfortunately this simple scheme is not adequate to explain the activity of alloys containing palladium (0.6 unpaired *d* electrons per atom). On this basis it would be expected that Pd-Pt alloys would show little variation in catalytic activity with composition, whereas Pd-Rh alloys would exhibit a maximum in activity similar to that found for Pt-Rh. Neither prediction is in accord with experimental observations (*2*) and in general palladium shows a much lower activity than expected from its electronic structure. The unusually low activity of palladium in exchange reactions has been noted before by Trapnell (*15*) and no satisfactory explanation appears to be available.

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