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Catalytic Activity of Noble Metal Alloys. Methane–Deuterium Exchange and Propane Cracking on Platinum-Palladium and Palladium-Rhodium Alloys

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The exchange reaction between methane and deuterium and the cracking of propane in the temperature range 100° to 200° have been used to study variations in catalytic activity in the Pt-Pd and Pd-Rh alloy series. Stepwise exchange was exhibited by both Pt and Pd, CH_3D being the most abundant initial product and the other deuteromethanes appearing in order. Rh showed predominantly multiple exchange at the higher temperatures with the initial appearance of CD_4. Stepwise exchange was the most important mechanism with all alloy samples although the contribution of multiple exchange increased with increasing temperature. The order of activity of the pure metals followed the sequence Pt > Rh > Pd at 150° for both exchange and cracking reactions and the binary alloys showed intermediate activities. A rough correlation between atomic radius and exchange mechanism was observed and the mechanism of the exchange reaction is discussed.

INTRODUCTION

The application of current theories of catalysis to alloy systems has frequently been hampered by the lack of reproducible data on well-defined systems. In particular, the complexity of the reaction chosen for the study of alloy catalysts has often added to the difficulties of interpretation. Thus, in spite of the considerable use of the decomposition of formic acid and the dehydrogenation of ethanol as test reactions for alloys, there is no general agreement on the detailed mechanisms of these reactions (*1*). It has recently been shown (*2*) that the exchange reaction between methane and deuterium possesses several advantages for this type of study. Thus the reaction proceeds rapidly on most metals in the temperature range 100° to 200°C, the products can be analyzed continuously and easily in the mass spectrometer, and the mechanism, though not completely understood, appears to be less complex than the reactions mentioned above.

Active metals appear to fall into one of two categories depending on the dominant mechanism for the exchange reaction. The most common type involves stepwise exchange or the replacement of one hydrogen of methane by deuterium at each residence on the metal surface. In this case, CH_3D is the most abundant initial product with the higher deuterated species appearing in order. On some metals, multiple exchange is predominant, more than one hydrogen atom being exchanged at a time, with the initial appearance of CD_4 and CHD_3. In other cases, both mechanisms appear to operate simultaneously. In a previous report in this series, it was shown that multiple exchange is generally favored by increasing temperature and in binary alloy series involving metals with different behavior, stepwise exchange tends to suppress the multiple exchange process. In the Pt-Ru alloy series, a maximum activity was found for alloys in the composition range 10–25% Ru. This paper summarizes the application of this technique to binary alloys in the series Rh-Pd and Pd-Pt, a comparison being made of the rate of exchange and the rate of cracking (demethanation) of propane at the same temperature.

METHODS

Catalyst Preparation

The alloys and elemental metal catalysts were prepared by reduction of chloride solutions of the appropriate metals with 5% sodium borohydride solution. The alloys generally coagulated readily and the products were washed thoroughly to remove traces of chlorides and borates. The catalysts were then dried in air at 120°, ground, and then reduced in flowing hydrogen at 300° for 3 hr. The catalysts were gray-black powders with surface areas in the range 3–10 m^2/g, as determined by the BET method.

Both the Rh-Pd and Pd-Pt systems form complete series of solid solutions over the whole composition range. Debye-Scherrer X-ray diffraction patterns confirmed that the products were homogeneous solid solutions, the lattice constants being intermediate between values for the pure metals given in the literature (*3*). However, owing to the small particle size of the samples (100–300 Å), the X-ray lines were somewhat diffuse. The compositions of the alloys were determined by X-ray emission spectroscopy using pressed wafers of the samples (*4*). Calibration curves for the two series were constructed using standard mixtures of the metallic blacks homogeneously mixed in a tetrahedral blender. Alloy compositions were determined to within ±2% by this method and the results agreed well with the values obtained from the measured lattice constants of the alloys.

Materials

The palladium chloride, rhodium chloride, and chloroplatinic acid used in the alloy preparation were Fisher purified reagents. Phillips "Research Grade" methane and propane were used in this work; these materials had purities of 99.57 and 99.99 mole %, respectively. The propane was condensed and fractionally distilled from a liquid nitrogen trap before being admitted to the apparatus. Deuterium was obtained from General Dynamics Corp., and was 96% pure (3% HD, 1% H_2). Hydrogen for reduction purposes was purified by passage through a palladium leak. Samples of CH_3D, CH_2D_2, CHD_3, and CD_4, used for calibration purposes in the exchange experiments, were obtained from Merck, Sharp and Dohme (Canada), Ltd., and had minimum purities of 98%.

Procedure

(a) **Exchange experiments.** The technique for measuring methane–deuterium exchange has been described previously (*2*). The experiments were carried out in a conventional vacuum system attached to a General Electric mass spectrometer of the Nier sector type, with 60-degree single focusing and 6-inch radius of curvature. An ionizing voltage of 70 ev was generally used and the composition of the gas phase in contact with the catalysts was determined from calibration curves of the individual deuteromethanes obtained over a range of pressure. Alloy samples weighing 1 g were evacuated to 2×10^{-6} mm in a vacuum system attached through a molecular leak to the ionization chamber of the mass spectrometer, the total volume of the gas phase over the samples being 16.0 ml. The catalysts were then treated with successive doses of deuterium until no hydrogen or water could be detected in the gas phase. The metal surfaces were at this stage saturated with deuterium, the volume chemisorbed being between 0.8 and 1.9 ml STP, depending on the surface area of the sample. After further evacuation, deuterium was allowed to stand over the catalysts and the pressure was then adjusted to 40 mm D_2; 80 mm of methane were then added and samples of the gas phase were analyzed at frequent intervals. The initial rates of formation of the deuteromethanes and the rate of disappearance of light CH_4 were used to calculate the rates of the exchange reaction. Measurements were normally continued for several hours until the gas phase had attained approximately constant composition. At the end of each exchange run it was always found that the catalysts could be completely reactivated by treatment with deuterium generally at 150°C. No change in the surface areas of the alloys was detected during the exchange experiments.

(**b**) **Propane cracking.** Measurements of the rate of cracking of propane on the alloy catalysts were made in the volumetric apparatus described previously (*5*). Alloy samples were sealed into the adsorption cell and reduced at 150° in a stream of pure hydrogen from a palladium thimble. Gold foil traps protected the catalysts from mercury vapor during the course of the measurements. A measured volume of propane, at an initial pressure of 20 mm, was allowed to stand over the catalyst samples for a period of 1 hr, the catalyst being kept at a temperature of 152 ± 1° and the increase in pressure over the alloy being measured with a wide-bore mercury manometer. The rate of increase in pressure was usually quite linear during this period. At the end of 1 hr a sample of the gaseous products was condensed in a demountable trap cooled in liquid nitrogen. The contents of the trap were then analyzed in an F and M Temperature Programmed Gas Chromatograph (Model 300), using a 4-ft Molecular Sieve 5A column. The partial pressure of methane in the gas phase was estimated from calibration curves and good agreement was found between this value and the total increase in gas pressure over the catalyst. Small amounts of ethane were also generally found in the products.

(**c**) **Surface areas.** The surface areas of the alloy samples were determined in the volumetric apparatus above, using the adsorption of nitrogen at —195°. Good agreement with the BET adsorption equation was usually obtained and a value of 16.2 Å^2 was used for the cross-sectional area of the nitrogen molecule. Surface areas were reproducible to within 10%.

RESULTS AND DISCUSSION

Activity in Pd-Rh Alloys

In order to calculate the rate constants for the exchange reaction, the first order equations developed by Kemball (*6*) were used in the form:

$$-\log_{10}(\phi_\infty - \phi) = k_\phi t/2.303\phi_\infty - \log_{10}(\phi_\infty - \phi_0) \quad (1)$$

where ϕ_0 and ϕ_∞ are the initial and equilibrium values of the parameter ϕ defined by

$$\phi = x_1 + 2x_2 + 3x_3 + 4x_4$$

where x_i is the percentage of the species $CH_{4-i}D_i$ present at time t.

The initial rate of disappearance of light CH_4 could be represented by a similar first order equation

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

x and x_∞ being the percentages of CH_4 present at time t and at infinity.

The ratio of the two first order rate constants $k_\phi/k = M$ is a measure of the number of H atoms being replaced by D in each molecule of CH_4 at the beginning of the reaction.

The rates of the individual stepwise and multiple exchange mechanisms, R_1 and R_2, could be estimated from the initial rates of formation of the deuteromethanes by means of the relations,

$$R_1 = d[CH_3D]/dt$$

and

$$R_2 = d\Sigma[CH_2D_2 + CHD_3 + CD_4]/dt$$

By means of these equations the activation energies for stepwise exchange, ΔE_1, multiple exchange, ΔE_2, and for the disappearance of light CH_4, ΔE_3, were determined from exchange measurements carried out at different temperatures and the contribution of each mechanism to the over-all reaction was estimated.

Data for the Pd-Rh alloy series are collected in Table 1, all these results being

TABLE 1

Methane–Deuterium Exchange on Palladium-Rhodium Alloys[a]

(1) Alloy comp. (wt %)	(2) Lattice const. (Å)	(3) Surface area (m^2/g)	(4) Temp. (°C)	(5) k (mole/sec g)	(6) M	(7) R_1/R_2	(8) ΔE_1	(9) ΔE_2 (kcal/mole)	(10) ΔE_3	(11) $\log_{10} A_3$ (molecules/sec cm²)	(12) $\log_{10} k$[b]
100 Pd	3.890	8.9	163	6.35×10^{15}	1.2	7.2	21.6	42.8	31.4	26.8	10.45
			189	4.9×10^{16}	1.3	1.8					
8.1 Rh	3.884	9.6	132	1.32×10^{15}	1.0	11.4	26.3	42	34.5	28.9	10.95
			173	6.92×10^{16}	1.3	1.9					
13.0 Rh	3.878	6.8	141	7.02×10^{15}	1.1	11.0	22.5	45.7	27.2	25.4	11.32
			172	7.1×10^{16}	1.7	1.5					
19.5 Rh	3.872	7.1	130	3.2×10^{15}	1.0	11.4	27.8	45.2	31.0	27.5	11.50
			167	8.3×10^{16}	1.5	1.7					
29.0 Rh	3.868	8.2	140	1.42×10^{16}	1.1	8.5	18.8	41.0	20.8	22.4	11.45
			173	9.2×10^{16}	1.9	1.2					
53.0 Rh	3.844	5.0	124	2.24×10^{15}	1.0	20.0	35.0	46	32.9	38.9	11.80
			142	1.37×10^{16}	1.0	7.8					
75 Rh	3.825	5.9	121	2.0×10^{15}	1.0	19.5	30.5	45	36.7	30.8	11.90
			145	3.03×10^{16}	1.1	5.7					
100 Rh	3.804	4.4	27	5.5×10^{12}	1.0	2					
			99	1.4×10^{16}	1.0	3.9					
			127	3.9×10^{16}	1.7	1.1	8.0	16.9	11.0	17.9	12.20
			137	5.1×10^{16}	2.5	0.7					
			151	8.0×10^{16}	3.4	0.5					
			156	8.8×10^{16}	3.6	0.2					

[a] One gram alloy samples; 80 mm CH_4 + 40 mm D_2 initially.

[b] 150°C.

obtained with a 1 g sample of alloy and an initial mixture of 80 mm CH_4 and 40 mm D_2.

In Table 1, Cols. 1 and 2 give the composition and lattice spacings, a_0, of the alloys. The surface area as determined by nitrogen adsorption is shown in Col. 3, and the temperature of the exchange runs in Col. 4. The initial rate of disappearance of light CH_4 is shown in Col. 5 in terms of the first order rate constant, k, as calculated from Eq. (2). The values of k in all cases lie between 10^{14} and 10^{18} molecules CH_4/sec g catalyst for exchange in the temperature range 100–200°. The ratios of the rate constants $k_\phi/k = M$ are given in Col. 6 and the ratios of the initial rates for the two processes R_1 and R_2 in Col. 7. Columns 8–10 record the values of the three activation energies discussed above and Col. 11 shows the values for the frequency factor $\log_{10}A_3$ associated with ΔE_3, in this case A_3 being expressed in the specific units molecules/sec cm² of catalyst surface. The final column in Table 1 shows values of the specific rate for the disappearance of CH_4, $\log_{10}k$, calculated at 150° using the experimental values of A_3 and ΔE_3. This column gives a measure of the change in exchange activity of the alloys with composition.

Typical product distributions vs. time

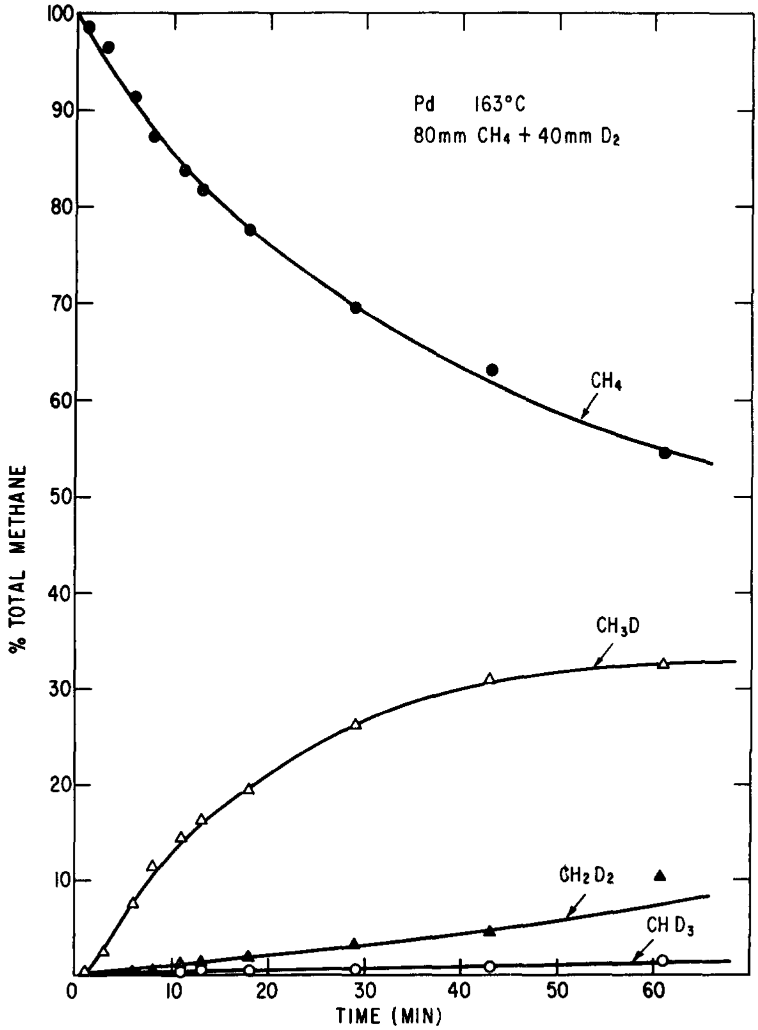


FIG. 1. Exchange of $CH_4 + D_2$ on palladium, 163°.

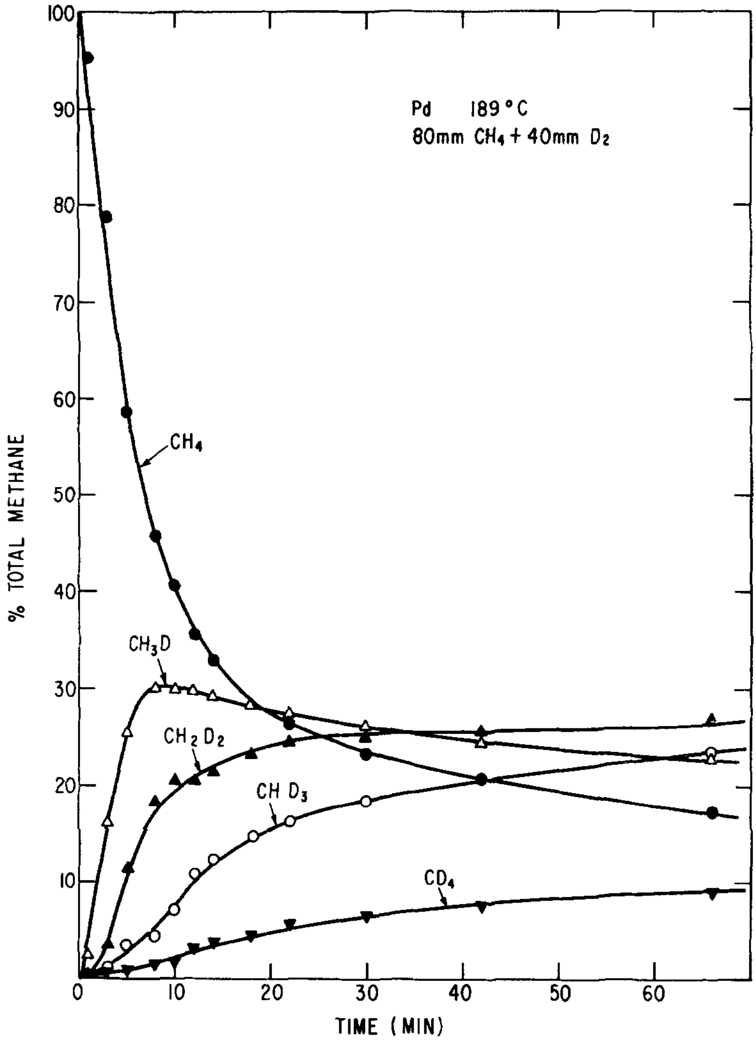


Fig. 2. Exchange of $CH_4 + D_2$ on palladium, 189°.

curves on a pure palladium sample are shown in Figs. 1 and 2. Stepwise exchange was the most important mechanism with this metal, as shown by the order of appearance of the deuteromethanes and the values of M and R_1/R_2 in Table 1. The value of the latter ratio decreased on increasing temperature, indicating increasing contributions from the multiple exchange mechanism. This is a general effect found for all the metals and alloys studied and is reflected in the greater value of ΔE_2 than ΔE_1 in all cases. For palladium, the difference between these two activation energies amounts to about 20 kcal/mole and although values for the frequency factors for the two mechanism were not computed, compensation was apparently not complete and a marked temperature effect was observed.

At the other end of the composition range in this series, rhodium showed mainly multiple exchange at the higher temperatures, the value of M increasing from unity at 99° to 3.6 at 156°. The increasing importance of multiple exchange is also illustrated in the results of Figs. 3–5, which represent the results of exchange experiments at progressively higher temperatures. In some cases, as shown in

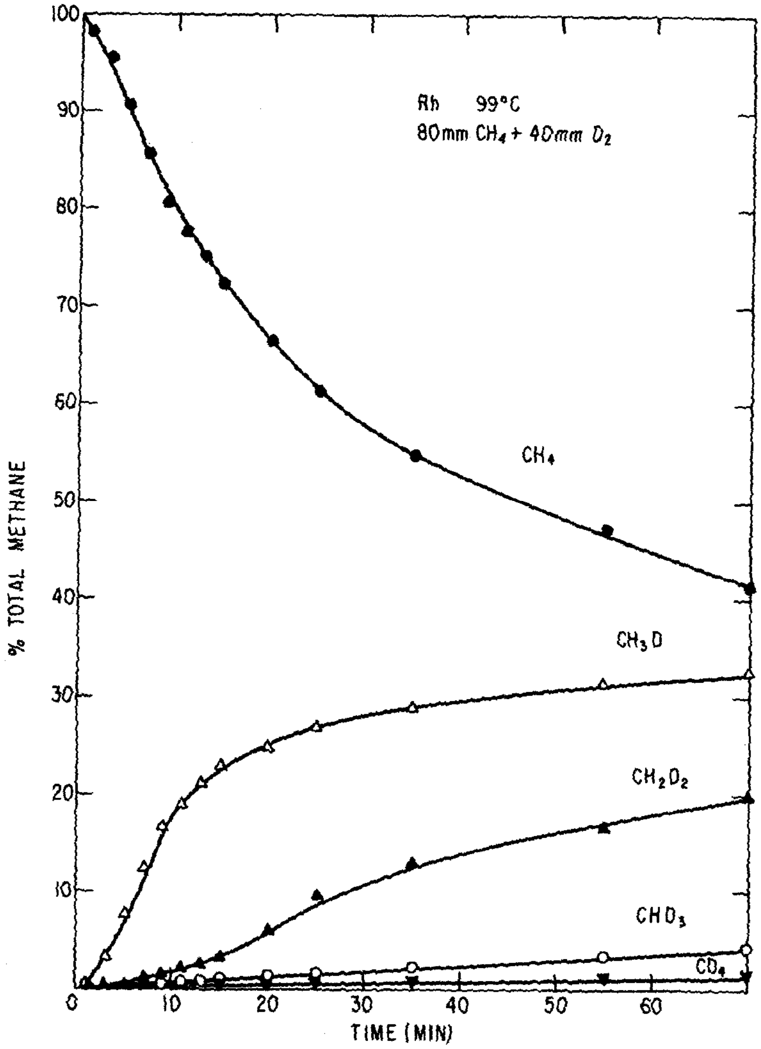


FIG. 3. Exchange of $CH_4 + D_2$ on rhodium, 99°.

Fig. 5, the concentration of CD_4 reached a maximum value and then decreased due to depletion of the deuterium content of the system. Arrhenius plots for the three processes on Rh are shown in Fig. 6. With this metal all three activation energies were substantially lower than the corresponding values for palladium.

Referring to the last column of Table 1, the specific activity of the alloys increased progressively on passing from Pd to Rh and no maximum similar to that found for the Pt-Ru system (*2*) was observed. With all alloy compositions except pure Rh, however, stepwise exchange was predominant, in spite of the fact that Rh showed considerably greater total activity than Pd. Typical results for a Rh-25% Pd alloy are illustrated in Fig. 7. This suppression of the multiple exchange process was observed also in the Pt-Ru system, in which case it was the least active metal which demonstrated the dominance of multiple exchange.

A plot of ΔE_3 vs. $\log_{10} A_3$, shown in Fig. 8, indicates that a well-defined compensation effect existed for this process. This implies that a temperature T' exists at

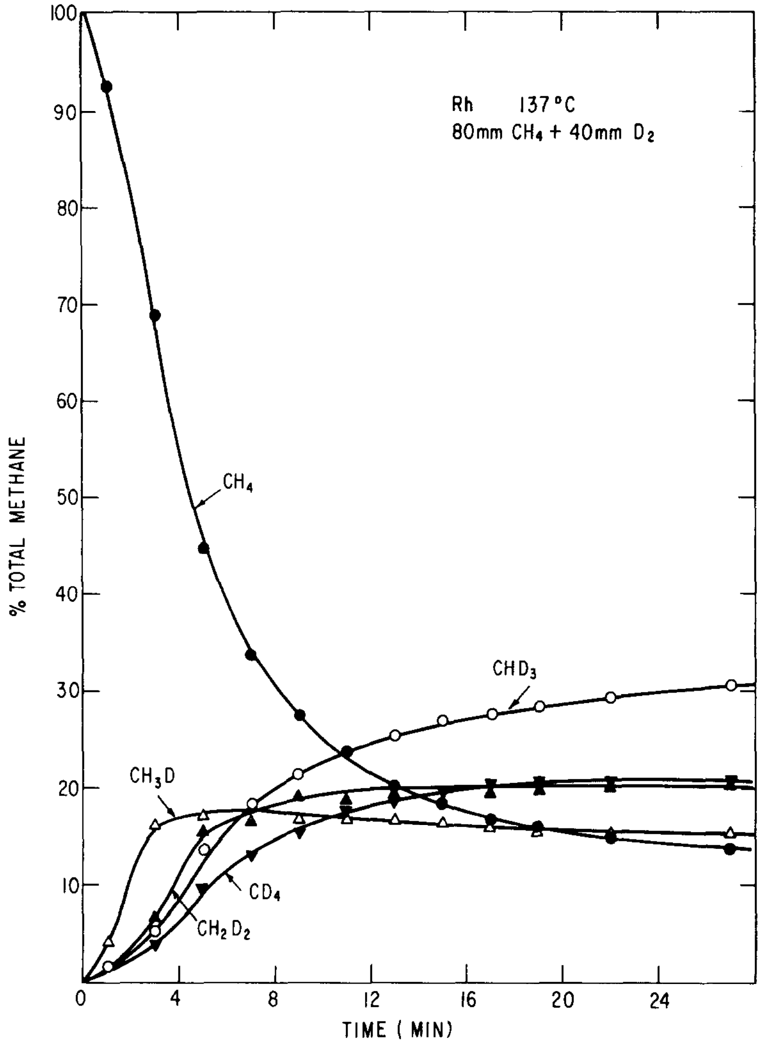


FIG. 4. Exchange of $CH_4 + D_2$ on rhodium, 137°.

which the rates of exchange on all samples in this series are equal (7). At this temperature, the rate log k' is the value of log A when the activation energy is zero. Hence,

$$(\log A - \log k') = m\Delta E = \Delta E/2.303RT'$$

where m is the slope of the line in Fig. 10.

For the Pd-Rh series, the value of $T' = 1/2.303\ mR$ was 203° (approx). Above this temperature, the order of activity of the alloys might be expected to be reversed. However, in view of the change in the nature of the exchange mechanism with increasing temperature, such an extrapolation might be unjustified. In spite of this compensation effect, there is no systematic variation in activation energy with alloy composition, the mean values for all samples except Rh being $\Delta E_1 = 26.1$; $\Delta E_2 = 44$; $\Delta E_3 = 31$ kcal/mole. The values obtained for Rh were considerably lower than those for all the other alloys. The specific rate for the exchange $\log_{10}k$ at 150° is plotted in Fig. 9 as a function of alloy composition.

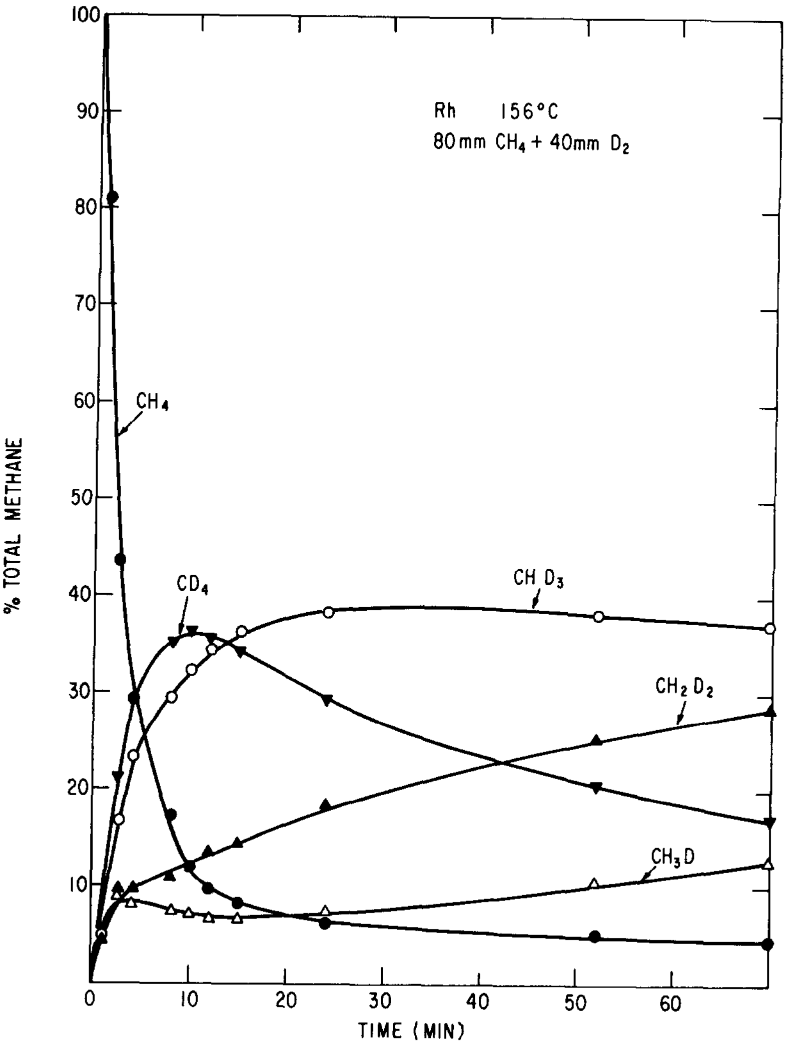


FIG. 5. Exchange of $CH_4 + D_2$ on rhodium, 156°.

Activity of Pd-Pt Alloys

In this case, both metals exhibit predominantly stepwise exchange over the temperature range studied, although Pd was considerably less active than Pt at all temperatures. Addition of Pd to Pt resulted in a progressive decrease in the activity of the alloys and no maximum was observed. Collected results for this alloy series are shown in Table 2 (p. 265), in which the symbols have the same significance as before. Again, increase in temperature resulted in a decrease in the ratio of the rates of the two processes R_1 and R_2, indicating that the small contribution of multiple exchange became more significant at higher temperatures. No progressive change in the activation energies was evident on passing up the alloy series, although pure Pt gave significantly lower values for ΔE_1, ΔE_2, and ΔE_3 than alloys containing Pd. This difference was not, however, as marked as with Rh and Pd. Average values of the activation energies were $\Delta E_1 = 28.5$; $\Delta E_2 = 40.1$; $\Delta E_3 = 31.2$ kcal/mole. A well-defined compensation effect was again observed between $\log_{10}A_3$ and ΔE_3, as shown in Fig. 10 and the value of the temperature

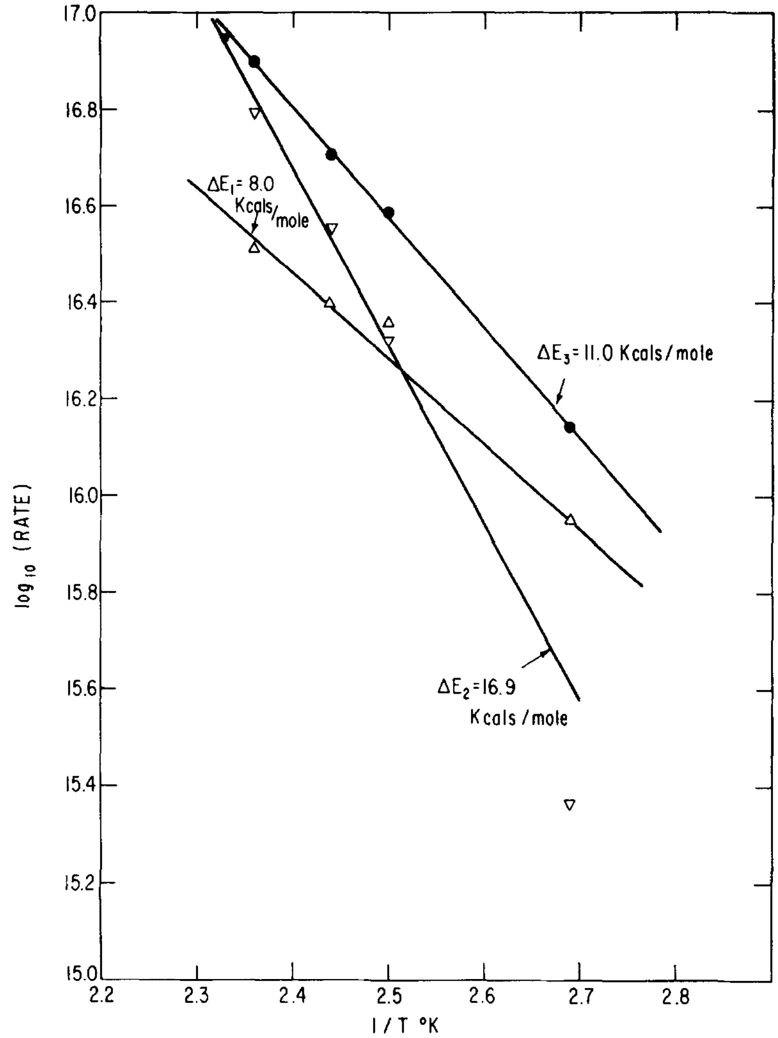


FIG. 6. Arrhenius plots for $CH_4 + D_2$ exchange on rhodium.

T' at which the rates on all samples became equal was about 307°. The variation of specific rate $\log_{10}k$ at 150° (k in molecules CH_4/sec cm^2) with alloy composition is shown in Fig. 10.

Propane Cracking

As the exchange reaction between methane and deuterium involves the dissociation of a C–H bond, it seemed of interest to compare the activity of the alloy catalysts for a reaction involving a C–C bond dissociation. The cracking (demethanation) of propane was chosen for this purpose as the reaction occurs readily in the same temperature range as that used for the exchange experiments and some information on the mechanism is available (*8*). As found previously (*9*) the products of cracking of propane on metals of the platinum group were methane, small amounts of ethane, and a carbonaceous residue of variable composition $(CH_n)_x$ which remained on the metal surface and tended to poison the catalyst. Hydrogen is occasionally formed in reactions of this type (*10*), but in the present work no hydrogen, olefins, or higher gaseous products were

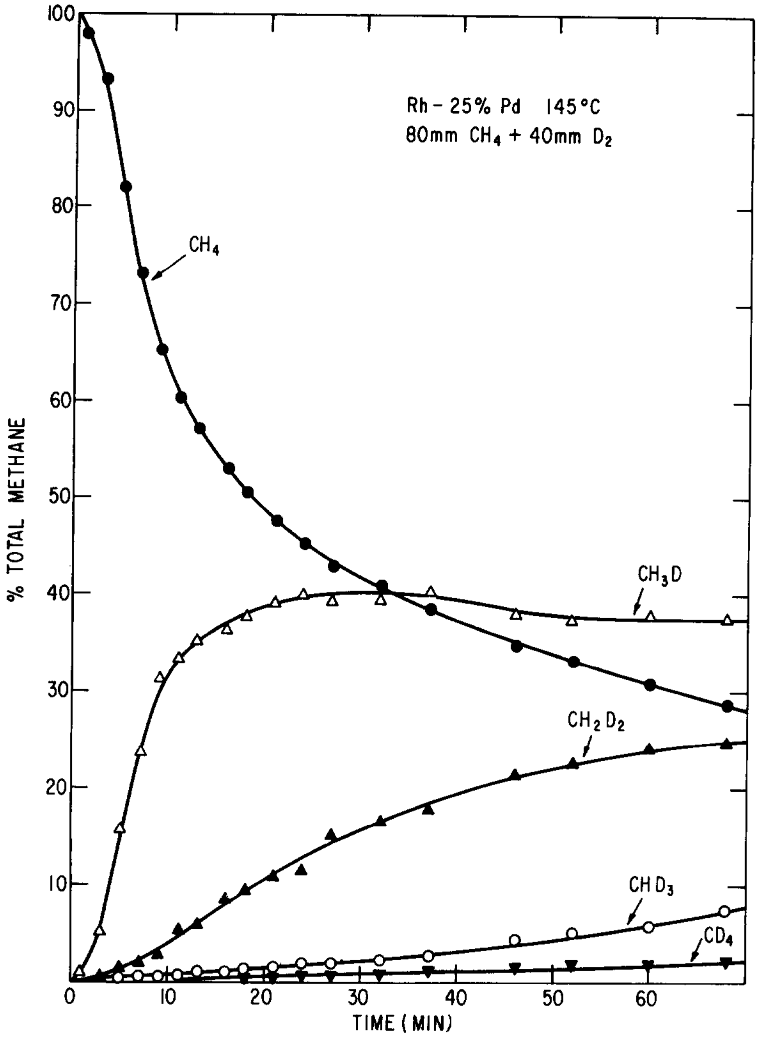


FIG. 7. Exchange of $CH_4 + D_2$ on Rh — 25% Pd, 145°.

detected. As it was found that the surface residues could not be completely removed by treatment with hydrogen at temperatures low enough to prevent further sintering of the alloys, fresh samples of catalyst were used for each determination. As the amount of ethane produced was small in every case, the activities of the alloys in this reaction were estimated from the volume of methane produced in 1 hr at 152°, using the same initial pressure of propane in each case. No attempt was made to determine the kinetics parameters and the results serve only as a rough comparison with the more detailed information obtained for the exchange reaction.

The variation of the specific rate $\log_{10}k'$ (k' expressed in molecules/sec cm^2) with alloy composition is plotted in Figs. 9 and 10 for the two alloy series. The rate of exchange was generally 5–10 times faster than the rate of cracking at the same temperature, although both rates are certainly dependent on the conditions of measurement and on the partial pressures of the reactants. Although the rates of both reactions vary in a similar manner with alloy composition, the rate of cracking seems to

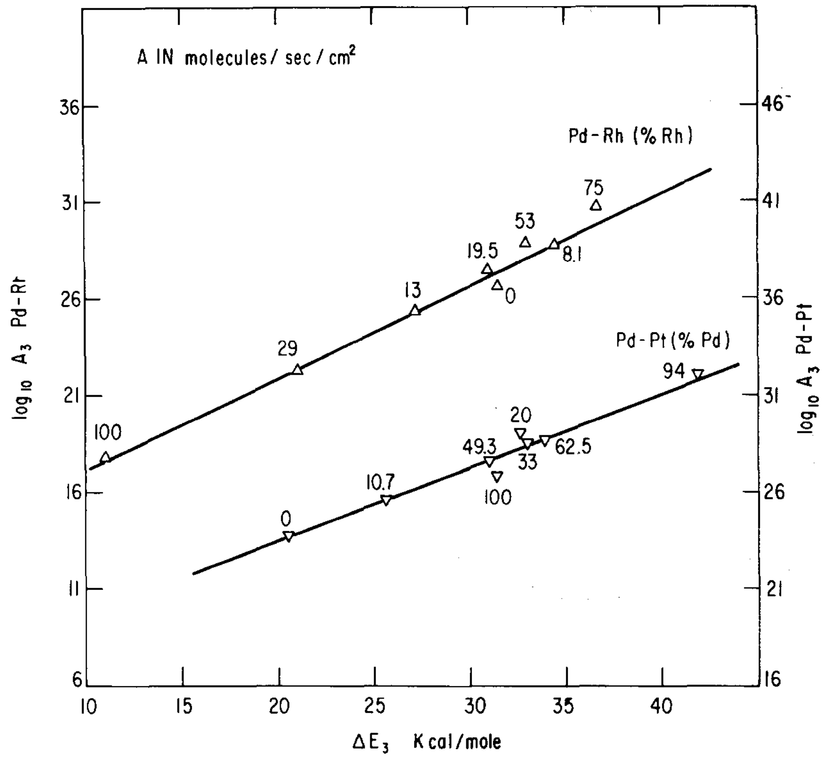


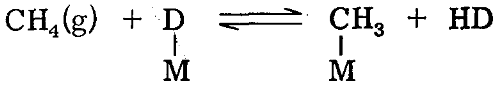
FIG. 8. Compensation effect for $CH_4 + D_2$ exchange on Pd-Rh, Pd-Pt alloys.

be less sensitive to small changes in alloy composition. In general, however, those metals which are most active for methane–deuterium exchange tend to show the highest activity for propane cracking also.

The specific activities of the pure metals for both the exchange reaction and for propane cracking followed the sequence $Pt > Rh > Ir > Ru > Pd$ at 150°, but differences in the kinetic parameters might cause changes in this order over a different temperature range.

Mechanism

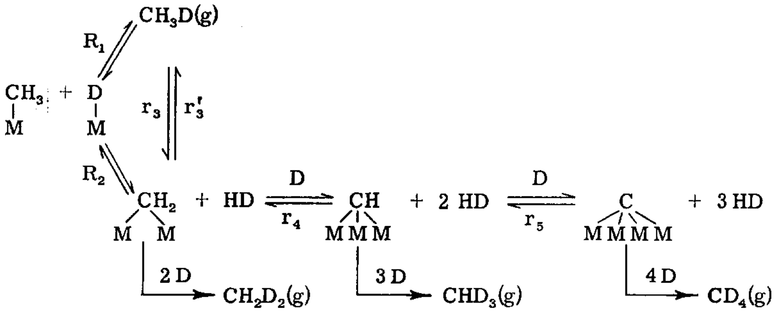
It seems reasonably certain that stepwise exchange proceeds via the initial dissociation of a C–H bond and the formation of chemisorbed methyl radicals on the metal surface. As the metal is initially covered with strongly adsorbed deuterium atoms, it is likely that this dissociation arises from a Rideal-Eley type of interaction between gas phase methane and surface D atoms,



$$CH_4(g) + \underset{M}{\overset{D}{|}} \rightleftharpoons \underset{M}{\overset{CH_3}{|}} + HD$$

The details of the mechanism of multiple exchange are, however, less clear, but the initially formed methyl radicals probably dissociate further into methylene or more highly dissociated fragments. A possible scheme in which both mechanisms can take place simultaneously is shown on p. 264. Rates of the individual steps are represented by R_i and r_j.

Metals, such as Pd and Pt, which favor stepwise exchange, have $R_1 > R_2$, and higher deuterated species would be formed by readsorption and dissociation of CH_3D via the steps r_3, r_4, and r_5. The rapid removal of methyl radicals from the surface as CH_3D would tend to suppress the initial appearance of higher deuterated products by the R_2 mechanism. Ru and Rh, however, have $R_2 > R_1$ and the small amounts of



CH_2D_2 formed in these cases suggest that the rates of steps r_5 and r_4 are substantially greater than R_2. By this means initially formed methyl radicals are rapidly converted to CD_4 and CHD_3 with the formation of only small amounts of CH_3D. The latter could, however, be produced by the recombination of surface methylene with HD by step r'_3. The tendency to form highly dissociated fragments will be expected to be favored by increase in temperature, leading to greater participation of the R_2 reaction.

Although it is likely that no single physical property of the metal is responsible for determining the mechanism of the exchange reaction, there seems to be a rough correlation between the type of

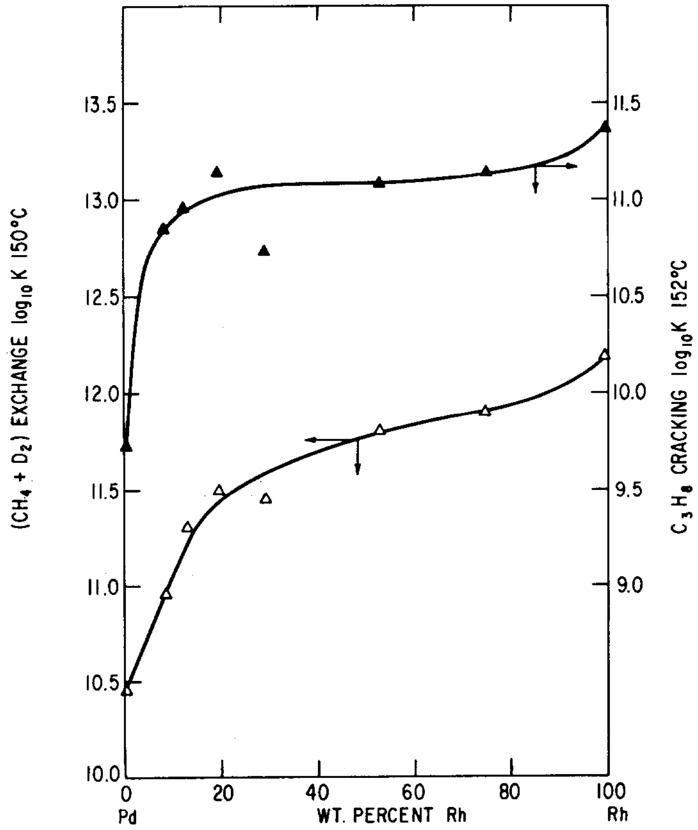


FIG. 9. $CH_4 + D_2$ exchange and C_3H_8 cracking on Pd-Rh alloys, 150°.

TABLE 2
METHANE–DEUTERIUM EXCHANGE ON PALLADIUM-PLATINUM ALLOYS[a]

(1) Alloy comp. (Wt %)		(2) Lattice const. (Å)	(3) Surface area (m^2/g)	(4) Temp. (°C)	(5) k (mole/sec g)	(6) M	(7) R_1/R_2	(8) ΔE_1	(9) ΔE_2 kcal/mole	(10) ΔE_3	(11) $\log_{10} A_3$ (molecules/sec cm²)	(12) $\log_{10} k^b$
100	Pt	3.916	4.9	83	5.0×10^{15}	1.3	6.1	20	26	20.5	23.6	13.1
				139	2.4×10^{17}	1.7	1.9					
10.7	Pd	3.912	3.2	138	2.17×10^{16}	1.1	3.9	28	36	25.6	25.5	12.3
				155	7.55×10^{16}	1.2	2.5					
20.0	Pd	3.904	3.6	119	1.3×10^{15}	1.1		26	36	32.6	28.8	12.0
				152	3.4×10^{16}	1.4	2.7					
33.0	Pd	3.899	3.3	140	4.13×10^{15}	1.0	11.6	30	42	32.9	28.6	11.6
				156	1.85×10^{16}	1.1	6.8					
49.3	Pd	3.894	6.0	138	8.65×10^{15}	1.1	7.3	30	45	31.0	27.6	11.5
				160	5.85×10^{16}	1.1	2.5					
65.2	Pd	3.892	6.2	134	1.92×10^{15}	1.0	14.2	30	45	33.8	28.7	11.3
				168	4.8×10^{16}	1.1	3.2					
94.0	Pd	3.890	3.8	140	4.48×10^{14}	1.0	13.4	42	48	41.8	32.1	10.6
				167	1.02×10^{16}	1.1	7.8					
100	Pd	3.890	8.9	163	6.35×10^{15}	1.2	7.2	21.6	42.8	31.4	26.8	10.45
				189	4.9×10^{16}	1.3	1.8					

[a] One gram alloy samples; 80 mm CH_4 + 40 mm D_2 initially.

[b] 150°C.

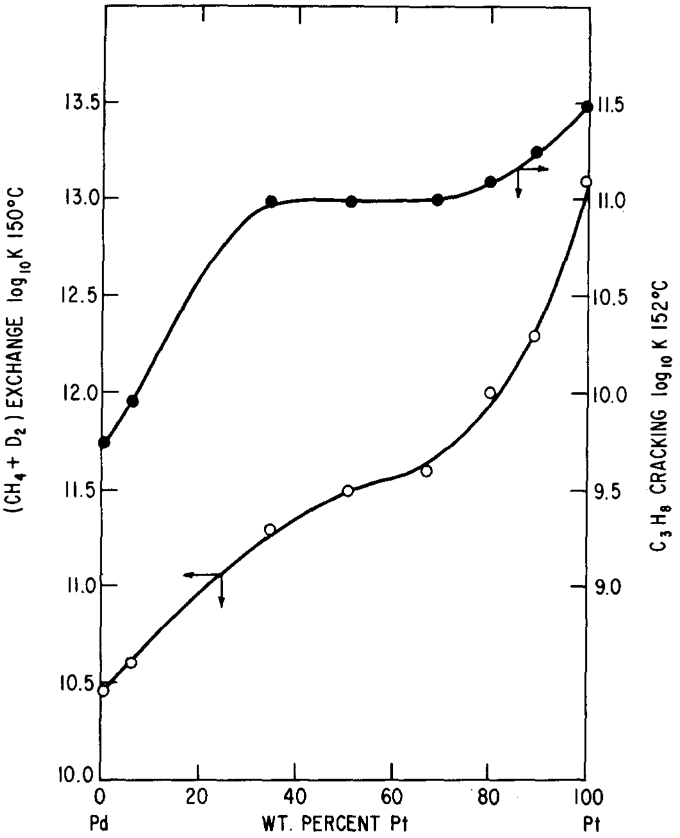


FIG. 10. $CH_4 + D_2$ exchange and C_3H_8 cracking on Pd-Pt alloys, 150°.

mechanism which predominates and the lattice parameters of the noble metals. As shown in Table 3, where values of the rate ratios, *M*, are compared with the lattice parameters, those metals which favor the multiple mechanism tend to have smaller atomic radii than those showing stepwise exchange. It is feasible that the formation of multiply-bonded surface radicals is favored by a high density of adsorption sites. It should be noted, however, that a similar correlation also exists between the values of *M* in Table 3 and the average number of unpaired "d" electrons, δ, per metal atom and it is not possible to decide whether geometrical or electronic factors are of most importance in determining the exchange mechanism.

On this basis it might be expected that the remaining metal in the platinoid series, Os (atomic radius 1.33 Å, $\delta = 2.2$), would exhibit multiple exchange, but no exchange results are yet available for this metal. Geometrical factors are likely to be more pronounced within a series of metals such as the platinum group where differences in heats of adsorption and electronic struc-

TABLE 3
LATTICE PARAMETERS AND EXCHANGE MECHANISM

Metal	Atomic radius	No. unpaired "d" electrons δ	*M* (150°)
		R_1 metals	
Pt	1.38 Å	0.6	1.7
Pd	1.37	0.6	1.1
		R_2 metals	
Ru	1.32 Å	2.2	3.5
Rh	1.34	1.4	3.4
Ir	1.35	1.7	3.0[a]

[a] Reference (*11*).

tures of the metals are minimal. In this connection a study of this exchange reaction on well-defined faces of single crystals of these metals would be most rewarding.

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