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NOTE

Deuterium NMR Spectroscopy Applied to the Products from Exchange of Cyclopentane on Metal Catalysts

The exchange reaction of cyclopentane with deuterium over metal catalysts was first studied over 30 years ago (*1, 2*) but it continues to pose problems and also provides new ideas about possible intermediates. Schrage and Burwell (*3*) showed that the reaction is complex and demonstrated that at least five distinguishable processes occur on palladium catalysts with the possible involvement of five different types of sites; the processes are the formation of the D_5-, D_8-, and D_{10}-compounds as initial products and two more leading to D_1- to D_3-compounds. A number of groups (*4–8*) have found metals, usually nickel or rhodium, which gave more D_2- than D_1-cyclopentane initially and there has been discussion as to whether the D_2-product is 1,2- or 1,1-exchanged. Another development has been reports (*9–12*) which claimed that D_4- and D_6-compounds are formed as initial products and suggested mechanisms which might account for these. The experiments which give such products were carried out at higher temperatures, usually 500 K or above, with either supported metal (Pt or Pd) catalysts or with alloy films formed from the combination of an active metal (Pt or Pd) with an inactive one (Au or Sn).

We have carried out experiments on the exchange of cyclopentane with deuterium on a number of catalysts using mass spectrometry to follow the reactions and then obtaining a detailed analysis of the groupings of deuterium atoms in the products by NMR spectroscopy in order to throw more light on the nature of the D_2-, D_4-, and D_6-products formed in systems similar to those mentioned above. The techniques have been described (*7, 13, 14*) and the approach depends on the ability to identify different groupings of deuterium atoms in cyclopentanes from the positions of the various resonances which are subject to known isotopic shifts caused by deuterium atoms near the deuteron under observation (*13*).

The Nature of the D_2-Product

Experiments were carried out using a previously described (*7*) Rh/SiO_2 catalyst, containing 10^{-4} mol metal g^{-1}, and a 5% Ni/SiO_2 catalyst (*15*) prepared from nickel nitrate and Aerosil 200 which after drying had been calcined in air at 823 K and was reduced at 773 K in flowing hydrogen for 1 h before evacuating and cooling to reaction temperature. Reaction mixtures contained 5 : 1 deuterium : hydrocarbon and the mass spectrometric analyses were made using 25-eV electrons to ionize the molecules. The composition of the products at the time when samples were taken for NMR spectroscopy are given in the upper part of Table 1. The line-narrowed NMR spectrum for the sample from Ni (run 2) is shown in Fig. 1. Peak A (δ = 1.492 ppm) corresponded to deuterium in the D_1-compound. The isotope shifts of −7.0, −17.4, and −52.7 ppb associated respectively with peaks B, C, and E enabled the main compounds contributing to each of these peaks to be identified using previous results (*13*) for the values of the various isotope shifts for deuterium atoms in cyclopentane. The main contribution to peak B came from the equivalent deuterons in 1,2-D_2-cyclopentane, each experiencing a β_{cis}-isotope shift of −7.0 ppb. The largest contributions to peak C were the five equivalent deuterons in the 1,2,3,4,5-D_5-compound, each having

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TABLE 1

Products from Exchange of Cyclopentane

Catalyst	Weight (W/mg)	Temperature (*T*/K)	Time (*t*/min)	% Alkane										
				D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
Low temperatures														
Rh	9	273	34	93.1	3.0	2.5	0.7	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Ni (run 1)	55	359	63	92.1	0.8	2.5	1.2	0.7	0.7	0.3	0.3	0.3	0.4	0.7
Ni (run 2)	106	332	93	91.8	1.5	2.6	1.2	0.7	0.8	0.2	0.2	0.2	0.3	0.5
High temperatures														
75 Pd/25 Ag[a]	26	664	129	91.7	0.4	0.8	0.6	3.1	0.4	1.7	0.0	0.1	0.3	0.9
				% Alkane				% Alkene				% Alkane		
				D_0	D_1	D_2		D_6	D_7	D_8		D_8	D_9	D_{10}
75 Pd/25 Ag	26	664	129	94.9	0.5	0.3		0.3	0.5	2.1		0.1	0.3	1.0
50 Pd/50 Ag	35	623	154	97.2	0.3	—		0.1	0.2	0.8		—	0.3	1.1

[a] Results worked out on the false assumption that all peaks were due to cyclopentanes.

a total isotope shift ($2\beta_{cis} + 2\gamma_{cis}$) of -17.8 ppb. If any 1,1-D_2-compound was present, the deuterons would also have appeared under the same peak since the α-isotope shift is -17.9 ppb. Peak E was largely due to the 10 identical deuterons in the D_{10}-compound (total isotope shift expected -52.9 ppb). Thus, in order to determine whether the D_2-product from Ni (run 2) was 1,2 or 1,1, it was necessary to compare the percentages of deuterium found in the various NMR peaks with calculated distributions derived from the mass spectrometric data. This comparison is shown in Table 2 and the evidence clearly favored the assignment of 1,2 to the D_2-compound. Similar agreement was found for the results from Ni (run 1). With the Rh experiment, the NMR spectrum gave only peaks in positions A and B and the insignificant amount of any peak in position C proved that no 1,1-product was formed.

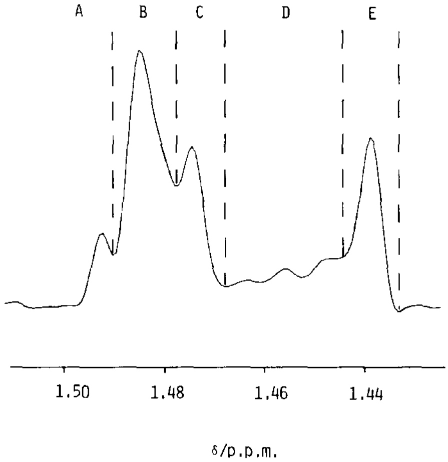

FIG. 1. The line-narrowed NMR spectrum for the cyclopentanes from Ni (run 2); see text and Table 2 for the description of the peaks and sections.

We conclude that the D_2-compound results from the reversible formation of $\alpha\beta$-diadsorbed (alkene) species and not through $\alpha\alpha$-diadsorbed (alkylidene) intermediates. This conclusion is in accord with views exposed in a number of papers (*4*, *13*, *16*) but contradicts the suggestion made by van Broekhoven and Ponec (*8*) that the D_2-product from the exchange of cyclopentane can be used as an indicator for the ability of a catalyst to form $\alpha\alpha$-diadsorbed intermediates. Nevertheless, we agree with van Broekhoven and Ponec that metals like nickel and rhodium are capable of forming such intermediates *at higher temperatures* from methane and other hydrocarbons even although the present results show that at low temperatures they give D_2-cyclopentane via alkene species.

TABLE 2

Correlation of NMR and Mass Spectrometric Results for Ni (Run 2)

NMR			Mass spectrometric		
Peak or section	Range of $-\Delta\delta$/ppb	% D	Contributions assuming that D_2 is 1,2	Calculated % D	
				D_2 is 1,2	D_2 is 1,1[a]
A	−5.0 to 2.0	6	D_1	5	5
B	2.0 to 15.0	42	$2D_2$, $3D_3$, $4D_4$	40	22
C	15.0 to 22.0	18	$5D_5$, $2D_6$, D_7	16	34
D	22.0 to 47.0	15	$4D_6$, $6D_7$, $6D_8$, $5D_9$	16	16
E	47.0 to 58.0	19	$2D_8$, $4D_9$, $10D_{10}$	23	23

[a] The contributions are as given in column 4 except that $2D_2$ is assigned to peak C not peak B.

Results at High Temperature

Two palladium–silver alloy catalysts, containing 75 or 50% Pd and described previously (*16*), were used to study the exchange of cyclopentane above 600 K and results are shown in the lower part of Table 1. Alternate methods of evaluating the mass spectrometric data are reported for the experiment with 75 Pd/25 Ag. The first assumed that only cyclopentane was present and gave a product distribution with substantial fractions of the D_4- and D_6-compounds and a ratio of D_4/D_6 of 1.8. The second assumed that ions with values of *m*/*e* from 74 to 76 arose from small amounts of highly exchanged cyclopentene, and gave the analysis shown in the penultimate line of Table 1 after making the appropriate fragmentation corrections. Results for the experiment with 50 Pd/50 Ag were evaluated by both methods but only the analysis from the second is shown.

NMR spectroscopy confirmed that highly exchanged cyclopentenes were present in both samples. Resonances with δ-values of 5.755, 2.622, and 1.765 ppm showed that deuterium was present in all three locations (olefinic, allylic, and remote) in cyclopentene and the relative amounts for 75 Pd/25 Ag were 1.2 : 2.0 : 1.0. A comparison of the δ-values with results for cyclopentene exchanged over calcium oxide (*17*) indicated that the cyclopentenes were heavily exchanged, in agreement with the mass spectrometric (MS) data. Furthermore, a quantitative comparison could be made by using both methods of analysis to work out R = (D in cyclopentane)/(D in cyclopentene). The NMR (MS) results for 50 Pd/50 Ag were $R = 0.51$ (0.60) and for 75 Pd/25 Ag, $R = 1.43$ (1.51).

The amount of cyclopentene (1.1%) observed over 50 Pd/50 Ag at 623 K agreed with the calculated value for thermodynamic equilibrium. The experimental value (2.9%) for 75 Pd/25 Ag at 664 K was lower than the calculated value (4.1%) but there was evidence of falling rates due to poisoning in that experiment.

We suspect that previous claims for the formation of D_4- and D_6-cyclopentanes as initial products from exchange reactions at 500 K or above are false and result from the neglect of alkene formation. The ratios reported for D_4/D_6 of >1 arise from the fragmentation of cyclopentene in the mass spectrometer. We found that the amount of the fragment ion, $C_5H_7^+$, from cyclopentene rises from 45% of the parent ion, $C_5H_8^+$, to over 210% as the voltage of the ionizing electron is increased from 10 to 25 eV. Thermodynamic considerations limit the amount of cyclopentene that can be formed. We estimate that 0.19% of cyclopentane could be converted to alkene at 500 K under the conditions used by McMahon *et al.* (*9*) and we note that these authors stated that the percentage of all products rose linearly with time except D_4 and D_6. The fact that cyclopentene, even although only present in a large excess of alkane, undergoes rapid and extensive exchange is interesting but agrees with previous results (*18*) over titanium dioxide (rutile) at high temperatures and more recent results with various alkene/alkane mixtures on platinum catalysts (*19*).

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