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Substituent Effects in Heterogeneous Catalysis

II. Deuteration of 2-Methylcyclohexanone over the Platinum Group Metals

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The catalytic reactions between 2-methylcyclohexanone and deuterium on platinum group metals were studied by means of mass and NMR spectrometry. Over Ru, Os, and Ir, only reduction to the corresponding alcohols occurred, brought about by simple addition of two deuterium atoms to the carbonyl bond. In contrast, over Rh and Pd, significant isotopic exchange at the C_2 and C_6 positions also occurred. The results over Pt were intermediate between these two groups. The axial and equatorial deuterium contents at each carbon position were also estimated for Rh and Pd. One characteristic feature was that, over Rh, the axial D content at C_6 is greater than that at C_2 and the reverse is true over Pd. A reaction mechanism for reduction and exchange is presented and discussed.

INTRODUCTION

In our previous studies concerning the mechanism of ketone hydrogenation we deuterated cyclohexanone (*1*) and 4-*t*-butylcyclohexanone (*2*). The unreacted ketone and the product alcohols were analyzed for deuterium incorporation by NMR and mass spectrometry. The use of paramagnetic shift reagents in NMR allowed us to determine the axial and equatorial deuterium contents at each carbon position of the cyclohexane ring. Based upon this stereochemical deuterium distribution data, the mechanism of ketone hydrogenation was discussed in some detail.

The present work is an extension of these tracer studies to 2-methylcyclohexanone (2-MCH). This ketone, because of its unsymmetry, provides an additional question which does not arise in the symmetrical ketones so far studied: Since the two α-carbons (C_2 and C_6) are not equivalent, it may well be asked which α position will be preferentially exchanged. In order to account for some unusual kinetic results in 2-MCH hydrogenation on Rh and Pd catalysts, we previously (*3*) speculated on the preferential formation of a C_1,C_2-diadsorbed species over a C_1,C_6-diadsorbed species as a reaction intermediate. If so, in 2-MCH deuteration on these metals, deuteriums would be brought to the C_2 rather than to the C_6 position.

EXPERIMENTAL

Apparatus. The glass reaction vessel previously described (*3*) was used for atmospheric deuteration, and a 100-ml autoclave was used for high-pressure deuteration. A Shimadzu Model GC-1C gas chro-

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matograph was used for the separation of reaction mixtures, and the separated peaks were analyzed with a Hitachi RMS-4 mass spectrometer and a Varian HA-100D NMR spectrometer.

Materials. The catalysts were prepared according to the procedure described before (*1*). Deuterium (99.9% pure) was purchased from Showa Denko, Ltd., and used as received. Cyclohexane (Wako "Tokkyu" grade) was also used as received. 2-MCH (Wako "Tokkyu" grade) was purified by washing with diluted sodium carbonate and water and then by drying over anhydrous sodium sulfate. The 2-MCH thus treated was further purified with a preparative gas chromatograph using a 3-m-long, 10-mm-i.d. column of 30 wt% PEG 20M on 30- to 60-mesh Chromosorb WAW at 155°C. Helium was used as carrier gas.

2-MCH deuteration. For atmospheric deuteration, a catalyst sample was weighed into the reaction vessel, and 10 ml of cyclohexane was added. The reaction vessel was flushed several times with deuterium and then charged with it at a reaction temperature of 30°C. Deuteration was started by adding 1.21 ml (0.01 mol) of 2-MCH via a syringe through the attached septum, immediately followed by shaking the reaction vessel. The reaction was continued until a conversion of some 30 or 70% was attained. The reaction mixture was collected, washed with saturated aqueous Na_2SO_4, and then separated by gas chromatography on a diglycerol column. Each of the gas chromatographic peaks, i.e., 2-MCH, *cis*- and *trans*-2-methylcyclohexanols (abbreviated to *cis*-2-MCHol and *trans*-2-MCHol), was subjected to mass and NMR spectrometry.

Deuterations at elevated pressures were conducted in the autoclave. A catalyst sample was weighed into it, and then 20 ml of cyclohexane plus 2.42 ml (0.02 mol) of 2-MCH were added. The autoclave was then flushed several times with deuterium, charged with it up to 20 atm, and subsequently immersed in a water bath maintained at a reaction temperature of 80°C. After thermal equilibrium was established with a pressure rise up to about 23 atm, magnetic stirring of the reaction mixture was started. The reaction was continued until an approximate conversion of 70% was attained, accompanied by a pressure decrease of 3 to 4 atm. The reaction mixture was separated and analyzed in the same manner as for the atmospheric deuteration.

Following the above procedures, several deuteration runs were conducted using different reaction conditions, which are listed in Table 1.

Mass spectrometry. The mass spectrometer was operated at a low electron-accelerating voltage of 8 V to minimize fragmentation. In the case of 2-MCH, the parent ion (P^+) was most abundant. Therefore, the isotopic distribution of 2-MCH samples was easily determined from the P^+ peak heights after suitable corrections for naturally occurring ^{13}C and ^{18}O by assuming an identical ionization probability for deuterated and undeuterated species. The isotopic distribution of the product alcohols was similarly determined based on the P^+ peaks. Although the P^+ peaks of many alcohol molecules are usually too low to be used for quantitative analyses, those of *cis*- and *trans*-2-MCHol were unexpectedly high, second to the corresponding $(P-18)^+$ peak: the relative intensity $P^+/(P-18)^+$ was ≈ 0.3 for *cis*-2-MCHol and ≈ 0.7 for *trans*-2-MCHol. The favorable high P^+ intensity is presumably due to the protection of the hydroxyl group by the bulky methyl substituent against dehydration leading to $(P-18)^+$ ions.

NMR spectrometry. As we reported before (*4*) the axial and equatorial deuterium contents at each carbon position of cyclohexanones and cyclohexanols can be estimated from lanthanide-induced shift (LIS) spectra in NMR. In brief the deuterium content at a certain carbon position is

TABLE 1

Reaction Conditions and Stereoselectivities

Run	Catalyst		Temperature (°C)	P_{D_2} (atm)	Time (min)	Conversion[a] (%)	*cis*[b] (%)
	Metal	Weight (mg)					
1	Ru	60	30	1	170	71	74
2	Rh	60	30	1	34	71	49
3a	Pd	200	30	1	36	30	52
3b	Pd	200	30	1	145	69	59
4	Os	50	30	1	20	74	70
5	Ir	60	30	1	137	66	61
6	Pt	20	30	1	540	66	76
7	Rh	20	80	23–19	30	71	63
8	Pd	50	80	23–19	29	67	73

[a] 100 (*cis*-2-MCHol + *trans*-2-MCHol)/(2-MCH + *cis*-2-MCHol + *trans*-2-MCHol).

[b] 100 *cis*-2-MCHol/(*cis*-2-MCHol + *trans*-2-MCHol).

estimated by comparing the LIS proton peak intensity at that position with the standard LIS proton peak intensity. Signal assignments were based on the combined data of multiplicity, δ value, and proton decoupling. LIS spectra of 2-MCH were taken using 25 μl of the ketone sample dissolved in 0.5 ml of CCl_4 containing either 55 mg of $Pr(fod)_3$ or 80 mg of $Yb(fod)_3$. Here fod represents the anion of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione. $Yb(fod)_3$-Shifted spectra were internally locked on tetramethylsilane (TMS), and all the protons were resolved except for partial overlap between the H_{4a} and H_{5e} signals. However, most of these signals were quite broad due to a large downfield shift and inappropriate for very accurate estimation of deuterium contents. On the other hand, $Pr(fod)_3$-shifted spectra were internally locked on benzene and involved three unresolved pairs: $H_{2a} + H_{6a}$, $H_{3e}+H_{4a}$, and $H_{4e}+H_{5e}$. However, these unresolved signals as well as the resolved ones (H_{3a}, H_{5a}, H_{6e}, and H_{methyl}) were usually sharper than the $Yb(fod)_3$-shifted signals and, hence, permitted more accurate estimation of deuterium contents. We adopted as the internal standard of proton estimation the H_{4e} intensity for $Yb(fod)_3$-shifted spectra and the H_{3a} or H_{5a} intensity for $Pr(fod)_3$-shifted spectra, based on the approximation that these intensities are unaffected by deuterium smear.

LIS spectra of *cis*- and *trans*-2-MCHol were taken using 50 and 100 mg of $Pr(fod)_3$, respectively, following a procedure similar to that for 2-MCH. As the internal standard for deuterium estimation, H_{4e} was chosen for *trans*-2-MCHol, and a series of unresolved peaks in the region of $\delta = -8$ to -9 (presumably due to H_{3e}, H_{4e}, H_{4a}, and H_{5e}), for *cis*-2-MCHol.

RESULTS

Mass Spectrometric Data

Table 2 summarizes the results for unreacted 2-MCH samples. As in our previous work on the deuteration of cyclohexanone (*1*) and 4-tert-butylcyclohexanone (*2*), Rh and Pd were remarkable for the extensive deuterium exchange. Extensive deuterium exchange over Rh and Pd is also confirmed in Table 3 which lists the isotopic distributions of the product alcohols. Pt also caused deuterium exchange, but to a much smaller extent. The *cis*- and *trans*-2-MCHols were essentially identical in isotopic distribution. This similarity between isomers has already

TABLE 2

Isotopic Analysis of Unreacted 2-MCH

Run	Catalyst	Percentage of each isotopic species								D_m[a]
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	
1	Ru	99.0	1.0	0	0	0	0	0	0	0.01
2	Rh	61.9	22.6	8.3	3.8	1.9	1.5	0	0	0.67
3a	Pd	45.6	42.1	10.7	1.4	0.2	0	0	0	0.68
3b	Pd	11.9	35.2	35.6	14.3	2.5	0.5	0	0	1.62
4	Os	99.9	0.1	0	0	0	0	0	0	0.00
5	Ir	99.3	0.7	0	0	0	0	0	0	0.01
6	Pt	84.3	14.9	0.6	0.2	0	0	0	0	0.17
7	Rh	89.3	6.0	2.3	1.2	0.6	0.4	0.1	0	0.21
8	Pd	1.6	14.8	43.1	37.3	2.9	0	0	0	2.26

[a] Averaged number of deuterium atoms incorporated into each 2-MCH molecule.

been reported for the deuteration of 4-tert-butylcyclohexanone by us (*2*) and of 2-methylcyclopentanone by Cornet and Gault (*5*).

Although Rh and Pd are both remarkable for deuterium exchange, a closer look at Table 2 reveals some distinctions between them. First, compared under identical reaction conditions (runs 2 and 3b; 30°C, 1 atm, ≈70% conversion) D_m, the average number of D atoms incorporated per molecule, is much greater for Pd than for Rh. The difference became even more pronounced at an elevated temperature and D_2 pressure (runs 7 and 8). Upon going to the elevated conditions, deuterium incorporation became more extensive on Pd (runs 3b → 8), while it was suppressed very much on Rh (runs 2 → 7).

Second, Rh and Pd are different in the pattern of distribution of exchange products: although D_m for Rh is much smaller than for Pd, the amounts of d_4 and more highly exchanged species for Rh are comparable with or even greater than those for Pd. It is to be noted that 2-MCH can accommodate only three α-deuteriums (one at C_2 and two at C_6), and therefore the formation of d_4 and of more highly exchanged species is indicative of deuterium smear to some carbon positions other than α. As a measure of deuterium smear for 2-MCH let us introduce a quantity d_s defined by

$$d_s(\text{ketone}) = 100 \sum_{n=4} (n-3)d_n / \sum_{n=1} nd_n. \tag{1}$$

This quantity would represent the amount of smeared non-α-deuteriums as a percentage of the total deuteriums incorporated into 2-MCH if the α-hydrogens are completely replaced by deuteriums. However, in usual cases it is very likely that there is a small amount of 2-MCH molecules which contains one or more non-α-deuteriums while the α-hydrogens are not yet completely exchanged with deuteriums. In Eq. (1) such non-α-deuteriums are either underestimated or not counted at all. Therefore, d_s values worked out using Eq. (1) are regarded as a lower bound to the real percentage of non-α-deuteriums. Similarly for both *cis*- and *trans*-2-MCHol, the extent of deuterium smear beyond the C_2 and C_6 positions can be estimated based on an analogous quantity,

$$d_s(\text{alcohol}) = 100 \sum_{n=5} (n-4)d_n / \sum_{n=1} nd_n. \tag{2}$$

Here the summation of the numerator

TABLE 3

Isotopic Analysis of the Product Alcohols

Run	Catalyst	2-MCHol	Percentage of each isotopic species									D_m
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
1	Ru	*Cis*	8.0	91.3	0.5	0.2	0	0	0	0	0	0.93
		Trans	9.9	89.6	0.4	0.1	0	0	0	0	0	0.91
2	Rh	*Cis*	33.6	47.2	11.7	4.3	1.7	0.8	0.4	0.2	0.1	0.99
		Trans	35.6	46.1	11.4	4.2	1.5	0.7	0.4	0.2	0	0.95
3a	Pd	*Cis*	54.0	35.2	8.7	1.5	0.4	0.1	0	0	0	0.60
		Trans	53.5	35.4	8.8	1.7	0.6	0.2	0	0	0	0.61
3b	Pd	*Cis*	34.5	38.4	19.9	5.9	1.1	0.2	0	0	0	1.01
		Trans	36.9	38.0	18.4	5.5	1.1	0.2	0	0	0	0.96
4	Os	*Cis*	6.7	92.8	0.5	0	0	0	0	0	0	0.92
		Trans	6.9	92.9	0.3	0	0	0	0	0	0	0.92
5	Ir	*Cis*	8.7	90.8	0.5	0	0	0	0	0	0	0.92
		Trans	8.5	90.9	0.6	0	0	0	0	0	0	0.92
6	Pt	*Cis*	17.9	76.3	5.6	0.2	0	0	0	0	0	0.88
		Trans	16.5	78.2	5.0	0.3	0.1	0	0	0	0	0.89
7	Rh	*Cis*	10.2	76.0	7.4	3.4	1.4	1.0	0.4	0.2	0	1.16
		Trans	11.8	76.5	7.1	2.5	1.0	0.5	0.3	0.2	0	1.10
8	Pd	*Cis*	8.2	22.5	29.7	25.6	10.6	2.8	0.3	0.2	0	2.19
		Trans	9.9	23.6	31.1	25.0	9.3	0.9	0.2	0.1	0	2.04

begins with $n = 5$ despite the 5 deuteriums per alcohol molecule being accommodated by the inner carbons (C_1, C_2, and C_6) and oxygen because all deuteriums in the OD groups are lost before spectral analysis through washing with saturated aqueous Na_2SO_4. The numerical values for d_s calculated from Eqs. (1) and (2) using the data of Tables 2 and 3 are listed in Table 4. Obviously, d_s for Rh is greater than for Pd.

NMR Data

Table 5 shows the stereochemical isotopic distributions, i.e., the axial and equatorial deuterium contents at different carbon positions, estimated from the LIS spectra. In the case of *cis*-2-MCHol, many attempts to resolve the overlapped H_{2a} and H_{6a} signals failed, and hence D_{2a} and D_{6a} are given only as their sum. A comparison of D_{2a} and D_{6a} gives the third distinction between Rh and Pd: Over Pd $D_{2a} > D_{6a}$ both for 2-MCH and *trans*-2-MCHol, but the reverse is true for Rh. Our expectation of preferential isotopic exchange at C_2 was not realized with either Rh or Pd. Rather,

TABLE 4

Lower Bound to Percentage Deuterium Smear beyond the C_2 and C_6 Positions

Run	Catalyst	d_s		
		2-MCH	*cis*-2-MCHol	*trans*-2-MCHol
2	Rh	7.5	2.8	2.1
7	Rh	8.2	2.0	1.6
3b	Pd	2.2	0.2	0.2
8	Pd	1.3	1.7	0.8

TABLE 5

Stereochemical Deuterium Distributions within Molecule for the Unreacted Ketone and Product Alcohols

Run	Catalyst	Sample	Deuterium content[a]					D_m	
			D_1	D_{2a}[b]		D_{6a}	D_{6e}	NMR[c]	MS[d]
2	Rh	2-MCH		0.10		0.34	0.23	0.67	0.67
		Cis-2-MCHol	0.63		(0.08)[e]		0.22	0.93	0.99
		Trans-2-MCHol	0.57	0.05		0.22	0.05	0.89	0.95
3a	Pd	2-MCH		0.33		0.19	0.25	0.77	0.68
		Cis-2-MCHol	0.16		(0.40)[e]		0.12	0.79	0.60
		Trans-2-MCHol	0.23	0.28		0.16	0.25	0.68	0.61
3b	Pd	2-MCH		0.71		0.53	0.43	1.67	1.62
		Cis-2-MCHol	0.26		(0.52)[e]		0.29	1.07	1.01
		Trans-2-MCHol	0.18	0.37		0.20	0.17	0.92	0.96
6	Pt	*Trans*-2-MCHol	0.80	0.05		0.08	0.00	0.93	0.89
7	Rh	2-MCH		0.07		0.09	0.12	0.28	0.21
		Trans-2-MCHol	0.90	0.00		0.05	0.10	1.05	1.10
8	Pd	2-MCH		0.89		0.72	0.74	2.35	2.26
		Trans-2-MCHol	0.66	0.66		0.44	0.35	2.11	2.04

[a] Symbol D represents the number of deuterium atoms at the position indicated by the subscript (a = axial, e = equatorial).

[b] The methyl substituent is assumed to be equatorial.

[c] $D_m(\text{NMR}) = (D_1) + D_{2a} + D_{6a} + D_{6e}$.

[d] Quoted from Table 2 or 3.

[e] $D_{2a} + D_{6a}$.

$D_{6a} + D_{6e}$ exceeded D_{2a} in almost all cases.

Table 5 also shows that in most samples the D_m value determined by mass spectrometry agrees closely with that determined by NMR, thereby the validity of the determination of stereochemical isotopic distributions is confirmed. However, the amount of deuteriums smeared beyond the C_2 and C_6 positions was probably insufficient to be detected by NMR.

DISCUSSION

Figure 1 illustrates a mechanism of 2-MCH hydrogenation by which we propose to explain in qualitative terms the data obtained by the present tracer experiments. This mechanism is divided into four regions.

Region I shows the simple stepwise addition of two hydrogen atoms to the adsorbed carbonyl linkage. In the case of deuteration, this step forms only the alcohol-d_2 in which the deuteriums are bonded to the C_1 and O atoms. This alcohol-d_2 will be detected as -d_1 when its hydroxyl deuterium is replaced by hydrogen before mass spectrometry as in the present work. Region II represents the backward dehydrogenation process from a half-hydrogenated state (I_σ) to carbon–carbon-diadsorbed species (II_2 or II_6), followed by the forward successive hydrogenation to the product alcohols (*cis*- and *trans*-2-MCHol). This process is responsible for deuterium incorporation into the C_2 and C_6 positions. Region I plus Region II is essentially the same as the mechanism we presented before for the hydrogenation of cyclohexanone (*1*) and 4-*t*-butylcyclohexanone (*2*). Region III is added in order to account for deuterium smear beyond the C_2 and C_6 positions observed on Rh and, to a lesser extent, on Pd. Region IV represents the two equilibrium steps between three different species all of which are π adsorbed on the catalyst. These equilibrium steps serve as an alternative to Region II in accounting for deuterium incorporation into C_2 and C_6. One can consult the work of Cornet and Gault (*5*) in considering the role of Region IV in ketone hydrogenation.

We believe Region I is operative on all the catalyst metals used. The reactions on Ru, Os, and Ir must be almost entirely limited to this region because on these metals practically no deuteriums entered into the unreacted 2-MCH and because the products *cis*- and *trans*-2-MCHol contained little or no d_2 and more highly exchanged species. The deuterium incorporation into the C_2 and C_6 positions observed with Rh, Pd, and Pt is attributable to Region II or IV or both. While we cannot be sure at this time which is the case, we are inclined to regard both regions as significant. The reasons for this inclination are as follows. (i) In order to account for deuterium smear beyond C_2 and C_6, Region III must be assumed to occur, and hence Region II appears to be an indispensable intermediate stage connecting Regions I and III. (ii) Many transition metals including Rh, Pd, and Pt promote not only hydrogenation but also dehydrogenation (*6*). Besides, these three metals are known to form a variety of π-coordinated compounds. Therefore, it seems quite reasonable to assume

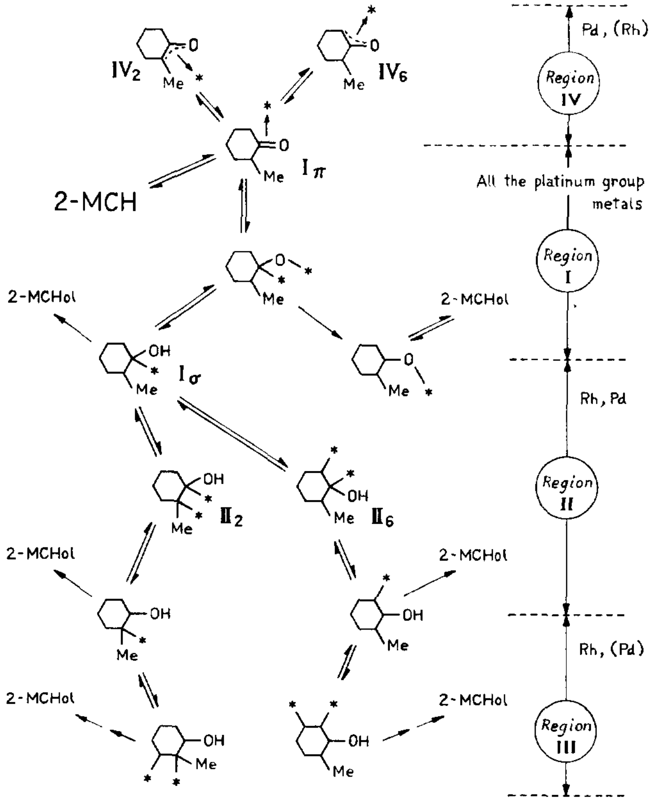

FIG 1. Mechanism of 2-methylcyclohexanone hydrogenation.

the formation of π-adsorbed IV_2 and IV_6 by hydrogen abstraction from I_π.

Now let us consider why the relative deuterium content at C_2 compared to C_6 $[D_{2a}/(D_{6a} + D_{6e})]$ is greater on Pd than on Rh. The relative importance of Regions II and IV is probably different for Rh and Pd: Since Pd is more apt to form π-coordinated compounds, the role of Region IV might be greater on Pd. With this in mind let us compare the two pairs of alternation steps, $II_2 \rightleftharpoons I_\sigma \rightleftharpoons II_6$ in Region II and $IV_2 \rightleftharpoons I_\pi \rightleftharpoons IV_6$ in Region IV. In each pair the methyl substituent must more or less hinder the formation of the subscript-2 species sterically, but hardly affect the formation of the subscript-6 species. Since in general π adsorption is much weaker than σ diadsorption, it is expected that the adsorbed substrate is closer to the catalyst surface in the $II_2 \rightleftharpoons I_\sigma \rightleftharpoons II_6$ alternation process than in $IV_2 \rightleftharpoons I_\pi \rightleftharpoons IV_6$. If so, the steric effect of the methyl substituent would be manifest more strongly in the $II_2 \rightleftharpoons I_\sigma \rightleftharpoons II_6$ process. In other words, a preference for II_6 over II_2 should be greater than a preference for IV_6 over IV_2, and this is the explanation why $D_{2a}/(D_{6a} + D_{6e})$ is greater for Pd than for Rh.

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