Substituent Effects in Heterogeneous Catalysis. VI. Competitive Hydrogenation of Methylenecyclohexane and 2-Methylmethylenecyclohexane over Platinum Group Metals

Kazuo TAYA, Shinya MORIMOTO, Chieko ABE, Kazumi NOMURA, Okio NOMURA,† and Kazunori TANAKA*,†

Tokyo Gakugei University, Koganei-shi, Tokyo 184

†*The Institute of Physical and Chemical Research, Wako-shi, Saitama 351*

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Methylenecyclohexane and its 2-methyl derivative were hydrogenated competitively in cyclohexane at 30 °C over platinum group metals. The methyl derivative was less reactive than the unsubstituted olefin on all the metal catalysts used. The reactivity of the methyl derivative relative to the unsubstituted olefin was not much different in going from one catalyst to another. However, Pd was unique in its very high activity for double bond migration. MINDO/2 calculations have revealed that the olefinic double bonds of the substituted and unsubstituted olefins are essentially identical in bond order but somewhat different in charge density. The observed methyl substituent effect is compared with that observed previously in hydrogenation of cyclohexanone and its 2-methyl derivative.

In a previous work[1] of this series, we conducted competitive hydrogenation of cyclohexanone and its methyl derivatives (2-, 3-, and 4-methylcyclohexanone) using group VIII metals as catalysts in order to study the substituent effects. All of the methylcyclohexanones were less reactive than cyclohexanone. Interestingly, the reactivity of a methylcyclohexanone relative to cyclohexanone could be correlated with the atomic radius of the catalyst metal: among those catalysts on which the same type of reaction scheme operates, the greater the atomic radius the greater the relative reactivity.

A question may now be raised: is this correlation confined to ketone hydrogenation alone or does it extend to include hydrogenation of other types of organic compounds such as olefinic and acetylenic species? The purpose of the present study is to investigate this question by means of competitive hydrogenation of methylenecyclohexane and its 2-methyl derivative. Since this olefin pair is a structural analog of the earlier studied ketone pair, *i.e.*, cyclohexanone and its 2-methyl derivative, the present study will be compared with the earlier one to see how olefin hydrogenation is different from or similar to ketone hydrogenation.

Table 1 lists the abbreviated notations used subsequently for the starting olefins, isomerized olefins, and hydrogenation products.

TABLE 1. NOMENCLATURE

Compound	In sentence	As subscript
(Starting olefins)		
Methylenecyclohexane	MeneC	A
2-Methylmethylenecyclohexane	2-MMeneC	B
(Isomerized olefins)		
1-Methylcyclohexene	1-MCene	
1,2-Dimethylcyclohexene	1,2-DMCene	
2,3-Dimethylcyclohexene	2,3-DMCene	
(Hydrogenation products)		
Methylcyclohexane	MC	P
cis-1,2-Dimethylcyclohexane	*c*-1,2-DMC	*c*-Q
trans-1,2-Dimethylcyclohexane	*t*-1,2-DMC	*t*-Q

Experimental

Catalysts. The Ru, Rh, Pd, and Os catalysts were prepared fresh from ruthenium trichloride, rhodium trichloride, palladium dichloride, and osmium tetraoxide, respectively, according to the procedure described in the previous paper.[1]

Two methods were used for preparation of the Ir catalyst. (a) It was prepared using iridium trichloride (Mitsuwa Kagaku Yakuhin, 99.9%) as the starting material according to the procedure described previously.[1] (b) A suspension of iridium tetrahydroxide (Mitsuwa Kagaku Yakuhin) in water was reduced at 100 °C for 20 min using an initial hydrogen pressure of 90 kg/cm^2 (1 kg/cm^2≈1 atm=1.013 $\times 10^5$ Pa). The resulting metal precipitate was washed repeatedly with water until the washings were neutral to Thymol Blue, dried under reduced pressure, and stored over silica gel.

The Pt catalyst was prepared by adding aqueous NaOH (10 wt%) in small portions to a stirred warm (60—70 °C) suspension of $PtCl_2$ (Koso Chemical) in water. The mixture was allowed to stand in that temperature range for half an hour. The resulting precipitate was filtered off, washed with water until the washings were neutral, and suspended in water. The reduction of this hydroxide suspension to a metal black was conducted in a glass reaction vessel at ambient temperature using hydrogen at atmospheric pressure. The resulting Pt black catalyst was washed and stored as described above for Ir catalyst (b).

Olefins. MeneC was either purchased from Aldrich Chemical Co. or prepared in our laboratory. The preparation of MeneC and 2-MMeneC was made using as the starting materials hexahydrobenzoic acid and its 2-methyl derivative, respectively. The procedure of Cope and Ciganek[2] was employed with slight modifications. One modification was the substitution of ether extraction for steam distillation in collecting *N,N*-dimethylcyclohexylmethylamine, one of the synthetic intermediates. Another important modification was made to the last stage of the synthetic procedure, *i. e.*, to the procedure for purifying the final product. In the original method, the crude MeneC was washed successively with diluted HCl, aqueous $NaHCO_3$, and with water. Because our preliminary experiment revealed that the alkali washing is prone to contaminate the final product with a trace of basic material (probably *N,N*-dimethylhydroxylamine), we

omitted this operation, and just repeated washing with water before and after HCl washing. The MeneC so prepared had a bp 101—102 °C with n_D^{25} 1.4472 (lit,[2] 102 °C, n_D^{25} 1.4474) and its yield was 18%. The 2-MMeneC obtained had a bp 126.5—128 °C with n_D^{25} 1.4510 (lit,[3] 124.5—124.8 °C/745 mmHg, n_D^{25} 1.4514) and its yield was 13%.

The 1,2- and 2,3-DMCene used as gas chromatography standards in identification of a few isomerized reaction intermediates were prepared from 2-methylcyclohexanone according to the method of Signaigo and Cramer.[4] In brief, 2-methylcyclohexanone was treated with the Grignard reagent CH_3MgI to form 1,2-dimethylcyclohexanol, and this alcohol was then dehydrated by distillation from anhydrous aluminum sulfate. The resulting olefin mixture of 1,2- and 2,3-DMCene and 2-MMeneC was fractionated between 110 and 140 °C. (lit,[3] bp 136.2 °C/745 mmHg for 1,2-DMCene and 130.3—130.7 °C/745 mmHg for 2,3-DMCene).

Procedures. Competitive hydrogenations were conducted according to a procedure similar to that used for the previous study[1] of competitive ketone hydrogenations. In brief, 10 ml of an equimolar solution of MeneC and 2-MMeneC (0.4 mol/l of each) in cyclohexane was placed, together with a weighed sample of metal catalyst (varying from 0.8 to 135 mg), in the glass reaction vessel — the one used in the previous study. The reaction vessel was further charged with an atmospheric pressure of hydrogen, and shaken at a reaction temperature of 30 °C. The reaction was followed volumetrically by measuring the hydrogen uptake and also gas chromatographically by analyzing aliquots of the reaction mixture at appropriate time intervals. The reaction temperature and hydrogen pressure were chosen to be identical with those in the earlier ketone study to permit direct comparison of both kinetic data.

Gas chromatography was carried out on a Yanako Model G 80 FID chromatograph using two columns in series (2.5 m ×3 mm i.d. 20 wt% trixylyl phosphate on Chromosorb W and 5 m×3 mm i.d. 30 wt% 3,3′-oxydipropionitrile on Chromosorb PAW at 65 °C). Base line resolution was obtained for all the peaks.

Two series of experiments were conducted using these procedures so as to measure R_B/R_A for all the catalyst metals in each series. In series I, both starting olefins MeneC and 2-MMeneC were prepared, stored in a refrigerator, and used without redistillation before use. In series II, commercial MeneC and prepared 2-MMeneC were used as the starting olefins. They were kept in the refrigerator and redistilled under nitrogen immediately before use. Ir catalyst (b) was employed in series I, and Ir catalyst (a) in series II.

Treatment of Kinetic Data

In this report we are dealing with competitive hydrogenation of the two olefins, *i.e.*, MeneC and 2-MMeneC. Let us assume that the reaction rate of each olefin is first order in the amount adsorbed, that the catalyst surface is bare in the presence of saturated hydrocarbons alone, and also that olefin adsorption obeys the Langmuir isotherm. These premises lead to the relative rate expression:

$$\frac{R_B}{R_A}\left(\equiv\frac{k_B K_B}{k_A K_A}\right) = \frac{d(C_{c-Q}+C_{t-Q})/C_B}{dC_P/C_A} \qquad (1)$$

where R is the reaction rate per unit concentration of A or B, k is the rate constant, K is the adsorption coefficient and C is the concentration. The subscripts are listed in Table 1. Let $C_{A(i)}$ and $C_{B(i)}$ stand for the initial concentrations of C_A and C_B, respectively. Neglecting double bond migration and any other side reactions,

$$C_A = C_{A(I)} - C_P \qquad (2)$$

and

$$C_B = C_{B(I)} - C_{c-Q} - C_{t-Q}. \qquad (3)$$

Inserting Eqs. 2 and 3 into Eq. 1 and integrating between the limits $C_P=0$ and C_P and between $C_{c-Q}+C_{t-Q}=0$ and $C_{c-Q}+C_{t-Q}$ yields

$$\frac{R_B}{R_A} = \log\left(\frac{C_{B(I)}}{C_{B(I)}-C_{c-Q}-C_{t-Q}}\right)\Big/\log\left(\frac{C_{A(I)}}{C_{A(I)}-C_P}\right) \qquad (4)$$

Results

Side Reactions. Over the VIII_3 metals (Os, Ir, Pt) little or no double bond migration occurred (always less than 1% of the conversion to the saturated products). Over Ru and Rh, double bond migration was appreciable but still less than 6% of the total MeneC conversion and less than 2% of the total 2-MMeneC conversion. In the case of Pd, double bond migration was even faster than hydrogenation at the initial stage. These results were not unexpected because group VIII_2 metals (Ru, Rh, Pd) were reported to be more active than group VIII_3 metals for double bond migration.[5-7] Especially in hydrogenation of 2-MMeneC with Pd, Mitsui *et al.*[8] observed, in accord with our experiments, isomerization/hydrogenation ratios of greater than unity.

Figure 1 shows a typical reaction profile on Pd. This result indicates that *endo*-olefins are much more slowly hydrogenated than *exo*-olefins.[9,10] The same tendency was observed with Ru and Rh.

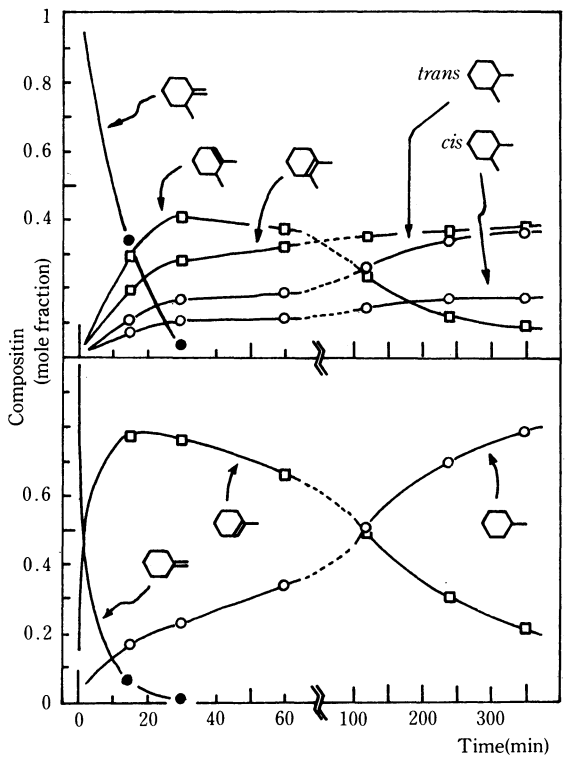

Fig. 1. Typical reaction profile on Pd.

Molar hydrogen uptake and molar olefin consumption were the same within experimental error for all the catalysts. This indicates that little or no hydrogenolysis occurred.

Substituent Effects. As in the earlier work on ketone hydrogenation, let us take the relative reactivity R_B/R_A as a measure of the methyl substituent effect. Except for Pd, the first-order log-log plots according to Eq. 4 were straight, and the R_B/R_A values were obtained from the slope of these plots. In an attempt to estimate the R_B/R_A values also for Pd, the sum $C_{c-Q}+C_{t-Q}$ was plotted against C_P and several slopes on that curve were inserted into Eq. 1 as the differential coefficient. The R_B/R_A values thus worked out, however, did not converge around a constant value.

Table 2. Substituent effect and stereoselectivity

Catalyst	R_B/R_A		*c*-1,2-DMC/*t*-1,2-DMC	
	Series I	II	Series I	II
Ru	0.19	0.14	1.7	3.6
Rh	0.26	0.21	1.1	3.2
Pd	—	—	0.6—0.7	0.5—0.7
Os	0.20	0.14	3.1	4.5
Ir	0.26	0.26	2.4	5.4
Pt	0.29	0.31	2.0	1.9

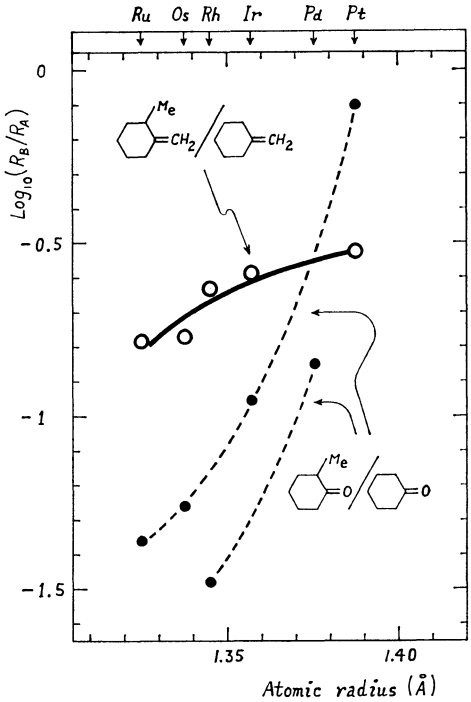

Fig. 2. Relative reactivity as a function of atomic radius of catalyst metal.

In series I, four or five competitive hydrogenation runs were carried out for each catalyst metal using different amounts of catalyst samples. In most cases, values of R_B/R_A for the same catalyst metal agreed within 8%, unless the catalyst amount was extremely small, say 2 mg or below. The experiments with such a small catalyst sample gave rise to either unusually high or low R_B/R_A values. In this case a sizable fraction of the catalyst surface may have been covered by some undetected impurities, and consequently the nature of the catalyst may have been altered so as to give such unusual results. Discarding the unusual R_B/R_A values, the others were averaged for each catalyst and are listed in Table 2. In series II, only one measurement of R_B/R_A was made for each metal catalyst using an appropriate amount of the catalyst. The values obtained are also listed in Table 2. For Ir and Pt, the agreement in R_B/R_A between series I and II is satisfactory. The cause of the small differences observed for the other metals is not clear.

In Fig. 2, the logarithm of R_B/R_A is plotted against the atomic radius of the catalyst metal,[11] where each of the R_B/R_A values is the average of the two values listed for each metal in Table 2. Figure 2 also includes for comparison the corresponding data for the earlier competitive hydrogenation of cyclohexanone and its 2-methyl derivative. It is seen that the $\log(R_B/R_A)$ values for the olefin system depends only slightly upon the atomic radius in contrast with a strong dependence of the ketone system. However, both olefin and ketone systems are alike in that the greater the atomic radius of the catalyst, the less negative is the value of $\log(R_B/R_A)$ or the less pronounced is the methyl substituent effect.

MINDO/2 Calculations. The charge densities and bond orders for MeneC and 2-MMeneC are basic to the understanding of the observed methyl substituent effect; they have been calculated using the MINDO/2 method on a Fujitsu computer Facom 230-75. It is very likely that MeneC is conformationally similar to cyclohexane, and that the chair form is its predominant ground-state conformation.[12] While definitive structural parameters for MeneC and 2-MMeneC are still lacking, a small difference from the cyclohexane skeleton would be expected because of the influence of the olefinic double bond. In particular, the bond angle C_2–$C_1(sp^2)$–C_6 in MeneC would be slightly larger than the cyclohexane C–C–C angle, 111.6°.[12,13] For our MINDO/2 calculations the following geometrical parameters were used for both MeneC and 2-MMeneC: angles 117° (C_2–$C_1(sp^2)$–C_6), 121.5° (C_2–$C_1(sp^2)$–$C_7(sp^2)$ and (C_6–$C_1(sp^2)$–$C_7(sp^2)$), 109.5° (for any other carbon set), 120° ($C_1(sp^2)$–$C_7(sp^2)$–H), 109.5° (H–C(sp^3)–H); distances 1.37 Å (C=C), 1.54 Å (C–C), 1.09 Å (C–H). The methyl substituent in 2-MMeneC was assumed to occupy the equatorial position. In order to define the rotational conformation of the methyl substituent, let us denote the three methyl hydrogens by H_α, H_β, and H_γ, with H_α representing the hydrogen that is taken as parallel to the axial C_3–H bond, and with H_γ representing the hydrogen that points away from the C_1=C_7 double bond. Were the six-membered ring of 2-MMeneC quite identical with that of cyclohexane, then the C_1–C_7–C_2 plane would bisect the H_α–C_8–H_β angle, and hence the distance H_α–C_7 would be equal to the distance H_β–C_7. However, owing to the widening of the C_2–C_1–C_6 angle and to the resulting structural deformation, C_7 should be closer to H_β than to H_α. The distances employed for MINDO/2 calculations

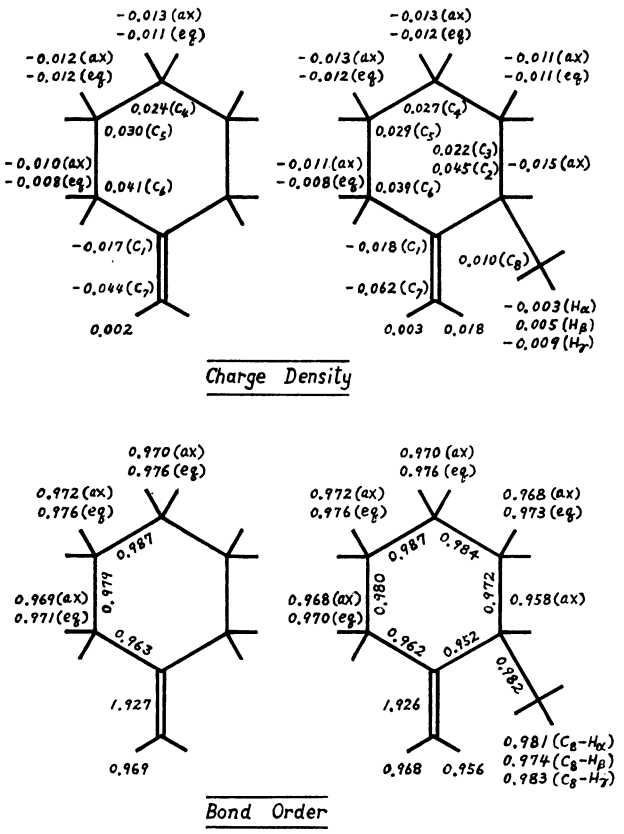

Fig. 3. Charge densities and bond orders for MeneC and 2-MMeneC.

were 2.26 Å for H_α–C_7 and 1.94 Å for H_β–C_7.

The results of the MINDO/2 calculations are shown in Fig. 3. Obviously, MeneC and 2-MMeneC are similar in bond order over the whole molecule, but dissimilar in charge density at and around the functional methylene group. The C=C double bond of 2-MMeneC is more negative and more polarized than that of MeneC. These results are reminiscent of a report of Libit and Hoffmann,[14] who made various molecular orbital calculations on propylene and toluene and showed that there is little net electron transfer from the methyl group to the ethylene or benzene but a significant polarization of the π electron system.

Other Data. Although not directly relevant to the substituent effect, the stereoselectivities measured in this study might be worth noting. Except for Pd, the observed isomeric ratios *c*-1,2-DMC/*t*-1,2-DMC were almost constant at conversions greater than 5%. The constant values are listed in Table 2. It is seen that except for Pd and Pt the absolute values for the isomeric ratio are considerably different between series I and II. However, the order of increasing *cis*/*trans* ratio in series I, Pd<Rh<Ru<Pt<Ir<Os, is not very much different from that in series II, Pd<Pt<Rh<Ru<Os<Ir, and these two sequences also resemble that observed by Nishimura and his associates, Pd≪Rh≈Ru=Pt<Os≈Ir.[15] Palladium is unique in that it produces more *trans* isomer than *cis*. Such *trans* selectivity on Pd was also reported earlier by others.[10,15]

Discussion

It might be worthwhile to make a few comments on Fig. 2 where a comparison is made of 2-methyl substituent effects between two structural analogs—MeneC and cyclohexanone. In the earlier ketone study, we could unambiguously rule out any polar factor because molecular orbital calculations have revealed that the carbonyl group of cyclohexanone and that of its methyl derivative are quite identical in charge densities and bond orders. In contrast, as seen in Figure 3, the olefinic double bond of MeneC is significantly different from that of 2-MMeneC in charge density. Thus, it is difficult to determine the main cause of the methyl substituent effect in the olefin system.

The present olefin system contrasts kinetically with the earlier ketone system in two respects; (i) with the exception of Pt, the olefin system is less negative in $\log(R_B/R_A)$ and (ii) the $\log(R_B/R_A)$ value depends only slightly upon the catalyst in the case of the olefin system, but very strongly in the case of the ketone system. Although more work is needed before these contrasts can be explained, the following matters may have some bearing. First, MeneC and its methyl derivatives are less flexible than their respective cyclohexanone counterparts.[16,17] Therefore, if the boat conformation play any role at all, this role would be more significant in ketone hydrogenation. Secondly, there can exist two distinct half-hydrogenated intermediates, *i.e.*, the C_1-metal- and C_7-metal-monoadsorbed species for olefins and the C_1-metal- and O-metal-monoadsorbed species for ketones. For either system, a larger substituent effect is expected when hydrogenation proceeds through the C_1-metal intermediate because the methyl substituent is closer to the catalyst surface on this intermediate. Thus, the substituent effect is probably influenced by the relative importance of these two intermediates. This relative importance may be quite different between olefin hydrogenation and ketone hydrogenation. Thirdly, the conformational equilibrium, *eq*-Methyl⇌*ax*-Methyl, is shifted further to the right in 2-MMeneC than in its ketone counterpart. Servies, *et al.*[18] experimentally determined the axial-methyl conformer content of 2-methylcyclohexanone to be 10.3% at 31.9 °C. On the other hand, Allinger *et al.*[13] calculated the enthalpy for the conformational equilibrium of 2-MMeneC (*eq*-Methyl⇌*ax*-Methyl) to be 0.50 kcal/mol. Assuming no entropy difference between the two conformers, this enthalpy value gives rise to an axial methyl content of 30.5% for 2-MMeneC at 31.9 °C. Finally, let us compare the C_1,C_7-diadsorbed olefin intermediate with its ketone counterpart, *i.e.*, the C_1,O-diadsorbed intermediate. Since the atomic radius of carbon is a little larger than that of oxygen, the C_7–metal bond in the adsorbed olefin must be a little longer than the O–metal bond in the adsorbed ketone.[19] Therefore, the 2-methyl substituent in the adsorbed olefin is expected to hang down a little further away from the catalyst surface compared with that in the adsorbed ketone. The further away the methyl substituent from the catalyst surface, the smaller

will be its hindrance to adsorption. This might be responsible in part for the less pronounced substituent effect in the olefin system compared with the ketone system on most of the catalyst metals.

Interestingly, Table 2 shows that the relative rate data are fairly reproducible on each catalyst despite large scatter in the *cis/trans* ratio data. This would mean that, compared to the relative rate, the *cis/trans* ratio is more profoundly affected by uncontrolled small variations of catalyst properties and environmental conditions, *e.g.*, change in surface structure due to aging and in minute traces of undetected impurities. The relative rate and the *cis/trans* ratio may be controlled by different steps of the overall hydrogenation pathway.

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