JOURNAL OF CATALYSIS **1**, 255–274 (1962)

The Catalytic Exchange with Deuterium of Polymethylcyclopentanes on Metal Films. Evidence for π-Bonded Intermediates

F. G. GAULT,* J. J. ROONEY, AND C. KEMBALL

From the Department of Chemistry, The Queen's University of Belfast

Received February 22, 1962

A new mechanistic theory has been developed to explain several reactions of hydrocarbons on metal catalysts. Interconversion can take place on the surface not only between σ-bonded monoadsorbed and diadsorbed intermediates but also between π-bonded species provided that the reactant hydrocarbons contain three or more adjacent nonquaternary carbon atoms. Evidence for this theory has been obtained by the catalytic exchange with deuterium of several polymethylcyclopentanes on films of rhodium, palladium, platinum, and nickel, using a mass-spectrometric analytical technique. Studies on *cis-trans* isomerization, followed by gas-liquid chromatography, have provided further support for the theory.

Palladium gave the most striking evidence for π-bonded intermediates. Rhodium was the most active metal for the exchange reactions and at low temperatures the role of σ-bonded intermediates was much greater than that of the π-bonded which only participated in the reactions at higher temperatures comparable to those needed to bring about exchange on palladium. The behavior of nickel and platinum was intermediate between that of rhodium and palladium.

Evidence is presented to show that on rhodium and nickel αα-diadsorbed intermediates permit the exchange process to propagate from the hydrogens on one side of cyclopentane rings to those on the other side. Platinum can cause exchange by αγ-diadsorbed intermediates at the same temperatures as required to form π-bonded species. Explanations are given for some apparently anomalous features of the distributions of deutero-compounds formed on rhodium.

The application of the theory to several aspects of the reactions of hydrocarbons on metal catalysts is discussed.

INTRODUCTION

The catalytic exchange of deuterium with hydrocarbons and other organic molecules on metals (*1*, *2*) has proved to be an extremely useful method of investigating the nature of the unstable intermediate surface compounds which are responsible for catalysis. Thus Anderson and Kemball (*3*) have demonstrated that the exchange of ethane on several metals can be explained by the interconversion of monoadsorbed ethane and 1,2-diadsorbed ethane.† This interconversion which is commonly referred to as the αβ process (*4*) was also shown to be important in exchange reactions of larger hydrocarbons, e.g., propane and isobutane on rhodium films (*5*) or propane on a variety of supported catalysts (*6*). The exchange of methane (*7*) and neopentane (*8*) on several metals showed that two-point attachment at one carbon atom (αα) to the surface was also possible but only took place at temperatures much higher than those required for the αβ process. Similarly, the exchange of neopentane (*8*)

---

* Present address: Faculté des Sciences—chimie génerale, Université de Caen.

† The terms monoadsorbed ethane and 1,2-diadsorbed ethane have a meaning analogous to chloroethane or 1,2-dichloroethane and refer, respectively, to chemisorbed ethyl radicals and ethylene molecules.

on rhodium films demonstrated that a 1,3-diadsorbed species ($\alpha\gamma$) could also participate in exchange but was more difficult to form than the other intermediates. In agreement with these conclusions were the results of Burwell and Briggs (*9*) who found that the exchange process of 3,3-dimethylhexane and 2,2,3-trimethylpentane with deuterium on a nickel-kieselguhr catalyst could not propagate past the quaternary carbon atom.

While these intermediates provide a satisfactory explanation for reactions of many hydrocarbons on metals, a new problem was revealed when Anderson and Kemball (*10*) exchanged cyclopentane and cyclohexane with deuterium on several metals. All the hydrogen atoms could be exchanged initially in these molecules on some metals and this could not be explained solely on the basis of the $\alpha\beta$ process. Burwell, Shim, and Rowlinson (*11*) found that optically active (+) 3-methylhexane racemized during the exchange process on several metals and again something more than an $\alpha\beta$ process is required in explanation. A related problem is that of explaining the hydrogenation of disubstituted cycloalkenes and benzenes to a mixture of *cis-* and *trans*-isomers of the corresponding saturated hydrocarbons. Hamilton and Burwell (*12*) have also drawn attention to the limitations of the $\alpha\beta$ process in explaining certain features concerning the isomerization of *cis*-but-2-ene to *trans*-but-2-ene on a palladium catalyst. These authors can be quoted as follows:

"It appears either that no completely satisfactory mechanism has been proposed or that some of the experimental data employed in mechanistic consideration are wrong."

Recent studies of the deuteration of cyclic olefins on iron films (*13*) and of the exchange of *n*-hexane with deuterium on palladium films (*14*) provided strong evidence for the conclusion that intermediates involving attachment at more than two adjacent carbon atoms to the surface could play an important role in catalysis by metals. In a preliminary report, Rooney, Gault, and Kemball (*15*) suggested that such intermediates are π-bonded to the metal surface in a manner which is closely similar to the nature of the bonding found in ferrocene and related organometallic compounds. These authors claimed that such π-bonded species were responsible for several phenomena of heterogeneous catalysis which have not hitherto been satisfactorily explained. As the concept is novel, it is necessary to explain the ideas upon which it is based in some detail.

There are two possible sources of limitation in the existing general mechanisms, one of which is the lack of consideration of possible intermediates involving more than two adjacent carbon atoms and the second is the absence of attempts at more exact definition of the bonds between the chemisorbed intermediates and the surface. This is because little is known about the bonding orbitals at the surface of solid metals but a fact which appears to have been overlooked is that the bonding orbitals of carbon atoms are well known and, therefore, there is a choice of possible σ-bonding by utilization of sp^3, sp^2, or sp hybridized orbitals, or π-bonding by utilization of p-orbitals. A detailed knowledge of the surface bonding orbitals is not required before the above statement is accepted, the only criterion being that such orbitals have the right symmetry in order to overlap with the orbitals of the carbon atoms and form a good bond. On this basis, one can examine more closely the nature of the bonding between adsorbed intermediates and metallic surfaces in a catalytic reaction.

Since only one atomic orbital in a state of sp^3 hybridization is involved in the bonding of an alkyl radical, the bond to the metal must be of the σ-type. A second bond to the surface from an adjacent carbon atom is also likely to be of the σ-type and tetrahedral geometry of all the bonds in the diadsorbed species may be assumed. Because of the carbon–carbon bond distance and the tetrahedral directions of the bonds to the surface, two metal atoms must be involved in this surface complex. There is also the possibility that such a diadsorbed species could be attached to the surface by an olefinic π-bond to one metal atom in a manner analogous to the bonding in ethylene platinous chloride. However, if such a species participates, it must interconvert with mono- and diadsorbed σ-bonded species and on the basis of energetic considerations is believed to be of little significance in exchange by an αβ process.

When an attempt is made to form a species with three σ-bonds at adjacent carbon atoms to three metal atoms, the geometric requirements become restrictive. In order that the bonds may be fairly free from strain the surface orbitals must be directed at the appropriate tetrahedral angles, the three surface atoms must be suitably spaced and the interatomic distance must lie within very narrow limits. Consideration of simultaneous attachment of four consecutive carbon atoms each by a σ-bond to a separate metal atom shows that the above restrictions become even more severe and, besides, the required atomic spacing is not normally encountered in transition metals. It is unlikely, therefore, that intermediates involving σ-bonds at more than two carbon atoms are important in reactions of hydrocarbons on metals.

However, there remains the possibility that a species involving attachment at more than two consecutive carbon atoms could be formed if there is a change to sp^2 hybridization. In this species, the carbon–hydrogen and carbon–carbon bonds at the carbon atoms in question become planar and the *p*-orbitals perpendicular to the plane form a π-bond by entering into a molecular orbital with suitable surface orbitals of the metal. The increase in energy required to bring about the hybridization change is offset by the delocalization energy of the π-electrons and the strength of the resulting bond. Bonding of this nature is believed to involve essentially only one metal atom because even from geometrical considerations attachment to more than one atom is prohibited. The *p*-orbitals are parallel to each other and at most can only be separated by 1.54 Å (carbon–carbon bond length) and the distance must be less because of the partial double-bond character. On the other hand, the shortest distance between two metal atoms in the transition series is greater than 2 Å. The type of bonding postulated is therefore closely similar to that found in ferrocene and related organometallic compounds and, recently, several π-allylic compounds have been described in the literature (*16*). The activation of the σ-bonded diadsorbed species to form a 3-carbon π-bond is believed to be the slow step in all interconversions of σ-bonded and π-bonded intermediates. Where the number of carbon atoms permits, interconversion of 3-carbon and 4-carbon π-bonded intermediates is believed to be rapid. The assumption that π-bonded species are attached to single metal atoms does not mean that geometrical factors are unimportant in relation to the specificity of various transition metal catalysts. These factors may influence the comparative ease of formation of σ-bonded and π-bonded intermediates and also the type of crystalline packing may govern the nature of the orbitals which the individual metal atoms have available for π-bonding.

A π-bonded intermediate (Fig. 1) is believed to be capable of reacting with hydrogen in two ways. In the diagrammatic representation, the *p*-orbitals are shown as broken lines and S means one surface atom. In the first reaction path, A, a surface deuterium atom adds below the planar center. In the second, B, a deuterium molecule reacts from above the planar center, one deuterium atom adding to the carbon atom and one being adsorbed on the surface. These additions can only take place at the outermost carbon atoms involved in the complex and they restore the sp^3-hybridization at the carbon atom concerned. Both processes must also be reversible in exchange reactions. The activation of molecular deuterium in this manner can be attributed in part to the residual bonding properties of the *p*-orbitals above the planar center and addition of this nature causes inversion of the carbon atom involved. There is also the possibility of the simultaneous addition of two deuterium atoms from a molecule to the upper side of the ring at adjacent carbon atoms.

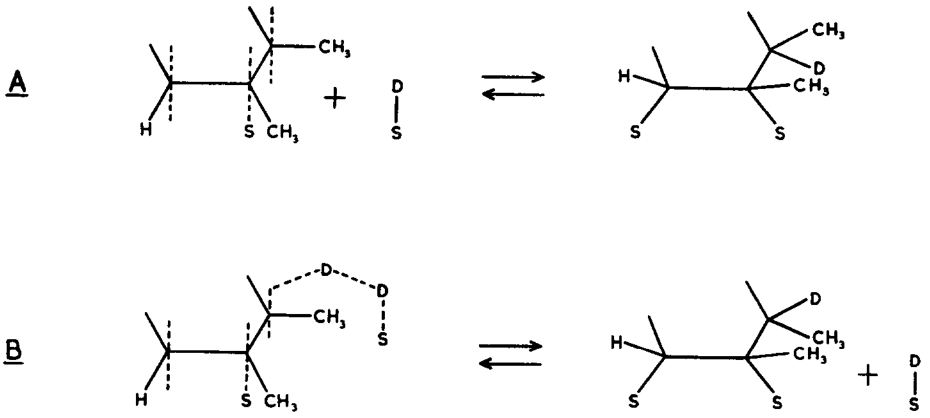
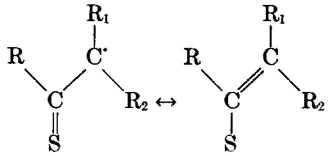


FIG. 1. Diagrammatic representation of π-bonded intermediates and the addition of deuterium to them.

Olefins are believed to be capable of reversibly adsorbing by loss of a hydrogen atom at the reactive allylic position with direct formation of a π-bonded species. The activated complex during the conversion of a σ-bonded diadsorbed species to a 3-carbon π-bonded species may involve an olefinic complex such as that already mentioned. Such an activated complex allows a possible route in getting from an adsorbed state involving two metal atoms to a π-bonded intermediate at one metal atom without having to postulate desorption of intermediate olefin. Aromatics and 1,3-dienes according to this mechanistic scheme can be adsorbed directly as π-bonded complexes.

The catalytic exchange of cycloalkanes (*10*) has shown that all the hydrogens in these molecules can be exchanged initially on metals such as palladium. This cannot be explained entirely by an $\alpha\beta$ process as this could only allow reaction of those hydrogens on the side of the rings directed towards the surface. The initial distributions usually show a break after the first group of hydrogens is exchanged and thus for cyclopentane there are maxima at the d_5 and d_{10} isomers. Increasing the reaction temperature causes the d_{10} maximum to increase relative to the d_5 maximum thereby demonstrating that an additional activation energy over and above that for the $\alpha\beta$ process is required before exchange propagates to the second group of hydrogens. It is clear that a second intermediate is involved and Anderson and Kemball (*10*) suggested that an $\alpha\alpha$-diadsorbed species would permit propagation. Burwell, Shim, and Rowlinson (*11*) suggested the following resonance hybrid as an intermediate in the racemization process during exchange. This species embodies the principle that a planar symmetrical center is



involved in racemization processes and a necessary condition for this symmetry is that the carbon atom concerned has sp^2-hybridization. However, this species is very unlikely since it requires considerable energy to form a free radical.

We believe that π-bonded intermediates are necessary to explain such problems. The object of the present work was to provide evidence for this concept by the catalytic exchange with deuterium of several hydrocarbons and at the same time to investigate the relative importance of π-bonded intermediates in reactions on several metals. Polymethylcyclopentanes were chosen because their cyclic structure allows a distinction between hydrogens on opposite sides of the rings and the inclusion of *gem*-dimethyl groups provides a method of blocking the propagation of exchange. For some of the compounds *cis-trans* isomerization is also possible and thus a second reaction could be studied simultaneously with the exchange reaction. The groups of hydrogens capable of being exchanged by formation of mono- and diadsorbed species [the basis for the classification of the hydrogen atoms in these groups is discussed in references (*1*) and (*11*)] and the total number expected to exchange by formation of π-bonded intermediates is summarized in Table 1, and a diagrammatic representation of the molecules is given in Fig. 2.

TABLE 1

Classification of the Hydrogen Atoms in the Substituted Cyclopentanes

	Compound	Groups of hydrogen atoms exchangeable by $\alpha\beta$ processes	Additional major initial products expected if π-bonded intermediates are formed
I	1,1,3,3-Tetramethyl	1,1,2,2	None
II	1,1,3,3,4-Pentamethyl	1,1,1,5	d_6
III	*trans*-1,1,3,4-Tetramethyl	1,1,5,5	d_{12}
IV	*cis*-1,1,3,4-Tetramethyl	1,1,10	d_{12}
V	*cis*-1,2-Dimethyl	3,11	d_{14}
VI	1,1,3-Trimethyl	1,2,7	d_{10}
VII	1,1,2,4-Tetramethyl	1,5,6(*trans*) or 1,1,10(*cis*)	d_{12}

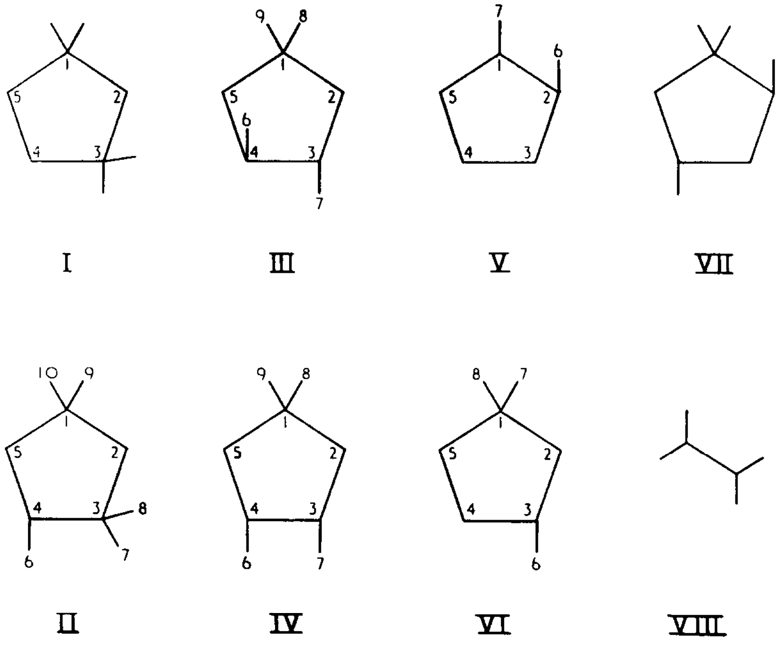


Fig. 2. Diagrammatic representation of the hydrocarbons; compound VII may be the *trans*-isomer as shown or the *cis*-isomer.

EXPERIMENTAL

The apparatus and the method of preparation of the films have been described previously (*7, 17, 18*). Platinum, nickel, and palladium wires of "spectrographically standardized" quality were obtained from Johnson Matthey and the rhodium wire was "pure" grade (99.7%). Deuterium was prepared by electrolysis of 99.95% heavy water and purified by diffusion through palladium.

Compounds I to VII (Fig. 2) were prepared from the appropriate pure ketones (*19*) by Grignard reactions with methyl iodide or by Wolff-Kishner reduction. Their physical constants were found to be identical to the values published by the American Petroleum Institute (Projects 43 and 44). Purity checks and other analyses were carried out using a "Pye Argon Chromatograph" with a column (4 ft) containing 10% by weight of silicone oil dispersed on Celite (100–120 B.S.S. mesh) operated at 50°C and using a flow rate of 50 ml/min. No impurities were detected in compounds I and II in this way but it is possible that the samples of these compounds retained traces of oxygen-containing impurities as they were obtained from residues of the final distillation in their preparation. Compound III contained 2% of compound IV and a corresponding percentage of III was present in IV. It was difficult to resolve IV and VII by gas chromatography and consequently VII may have contained some IV in addition to 1% of III. An estimate of the amount of VII in IV was possible after a sample had been subjected to *cis-trans* isomerization because the peak due to the small quantity of the *cis*-isomer remaining was partly resolved into two peaks which indicated the presence of up to 15% of VII in IV. Two different samples of IV were used; the first obtained, like I and II, from a residue may have held traces of oxygen-containing compounds and the second, designated IV* was the last fraction of the distillation. Compound V was apparently pure when examined by gas-liquid chromatography but after *cis-trans* isomerization an impurity (7%) which was believed to be ethylcyclopentane was detectable. No impurities were detected in VI and the absence of any significant quantities of isomers without the *gem*-dimethyl group was confirmed by mass-spectrometric analysis and similar tests were made on compounds I, II, III, and IV. Compound VIII was obtained from L. Light & Co. All the hydrocarbons were stored over anhydrous calcium chloride and thoroughly outgassed before use.

The reaction mixtures for use with nickel, platinum, and rhodium contained about 1 mm of hydrocarbon and over 10 times as much deuterium. The pressures were measured at 0°C and so the reaction vessel (196 ml) contained about 7×10^{18} molecules of hydrocarbon. For reactions on palladium which occurred at higher temperatures, 2 mm of hydrocarbon were used in each reaction mixture.

The mass-spectrometric analysis of compound V was obtained from the peaks of the parent ions. As molecules with *gem*-dimethyl groups give extremely small parent peaks, the pseudoparent peaks corresponding to the loss of a methyl group were used for analysis and this method was also preferable for compound VIII as well. In each case, the usual corrections were made to allow for the naturally occurring heavy carbon and deuterium and for the formation of a single fragment ion involving the loss of one hydrogen or deuterium atom from the pseudoparent or parent molecules. These corrections for the formation of fragment ions were made on a statistical basis and were small as the ions amounted to less than 2% of the amounts of the pseudoparents except for VIII (4.6%) and for V (9.1% of the parent ions). The standard voltage for the ionizing electrons was 18 volts but this was raised for II (30), V (37.5), and VIII (40).

Kinetic Measurements

Two methods of analyzing the experimental data were used (*1*). The rate constant k_H for the disappearance of the light isomer was obtained by assuming that the reaction followed first order kinetics. Values of the initial rate in %/min were used to compare the relative activities of the different metals.

The second rate constant k_ϕ, representing the initial rate of entry of deuterium atoms into 100 molecules of hydrocarbon, was evaluated from the equation

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

where $\phi = \Sigma i\, d_i$, d_i being the percentage of the hydrocarbon present as the isotopic species containing i deuterium atoms at time t, and ϕ_∞ is the equilibrium value. For slow reactions Eq. (1) simplifies to

$$\phi = k_\phi t \quad (2)$$

The mean number of deuterium atoms entering each reacting molecule is given by

$$M = k_\phi/k_{\mathrm{H}} \quad (3)$$

but values of M could also be obtained directly from the initial distributions of products.

Investigation of cis-trans Isomerization

Gas-liquid chromatographic analysis was carried out on the reaction products after the exchange reaction had been followed for a known period. The exchange reaction was stopped by surrounding the reaction vessel by liquid air. Permanent gas, i.e., the hydrogen-deuterium mixture, was pumped away and the hydrocarbon was warmed to room temperature and then condensed in a detachable side tube which had been previously evacuated. An alternative procedure of expanding from the reaction vessel to the cooled side tube before removing the permanent gases was also used in order to avoid contact of the hydrocarbon with the catalyst in the absence of deuterium. The hydrocarbon (~1 mg) was dissolved in 100 mg of solvent (e.g., *n*-pentane) and samples of the solution taken up in glass capillaries were injected into the chromatographic column. The *cis* and *trans* isomers of the 1,2-disubstituted cyclopentanes were readily resolved and the accuracy of the analyses were ±1%.

RESULTS

Compound I—1,1,3,3-Tetramethylcyclopentane

Various initial distributions of products for the exchange of this compound are given in Table 2, which like later tables also contains some distributions after a considerable amount of the d_0 isomer had disappeared. Four hydrogen atoms, clearly those attached to carbon atoms 4 and 5 (Fig. 2), were more readily exchanged than the remainder in this molecule. After 90% of the d_0 isomer had disappeared over platinum or rhodium at 30°C, more than 80% of the products were in the range d_1 to d_4. The rapid equilibration of the first four hydrogen atoms on rhodium at 30°C is shown graphically in Fig. 3 where

TABLE 2
INITIAL AND OTHER DISTRIBUTIONS OF PRODUCTS FOR THE EXCHANGE OF 1,1,3,3-TETRAMETHYLCYCLOPENTANE (I)

Catalyst Temp. (°C)	Pt 0°	Pt 30°	Pt[a] 30°	Pd 75°	Ni 144°	Rh 0°	Rh[b] 31°	Rh[a] 30°
d_1	72	60.5	18.8	43	36	17.5	6	4.9
d_2	28	34.3	27.1	57	13	61	28	19.1
d_3	<1	3.0	25.0	<1	6	6	21	23.3
d_4	—	1.7	19.2	—	45	15.5	43.5	49.1
d_5	—	0.5	7.7	—	<1	<0.1	1.1	2.9
d_6	—	—	1.9	—	—	—	0.35	0.6
d_7	—	—	0.3	—	—	—	0.05	0.1
M (init. dist.)	1.28	1.47	—	1.57	2.6	2.2	3.05	—
M (Eq. 3)	1.24	1.49	—	1.60	—	2.4	3.05	—

[a] Distribution when d_0 had decreased to 10%.

[b] Distribution at $t = 0.5$ min ($d_0 = 81.6\%$).

$$\phi_1 = \Sigma_1^4\, id_i' \text{ and } \phi_2 = \Sigma_5^{15}\, id_i$$

are plotted against time, d_i' representing the percentage of isotopic species based on $\Sigma_0^4 d_i' = 100$.

was greater over platinum than rhodium and must represent the exchange of hydrogen atoms in one of the *gem*-dimethyl groups.

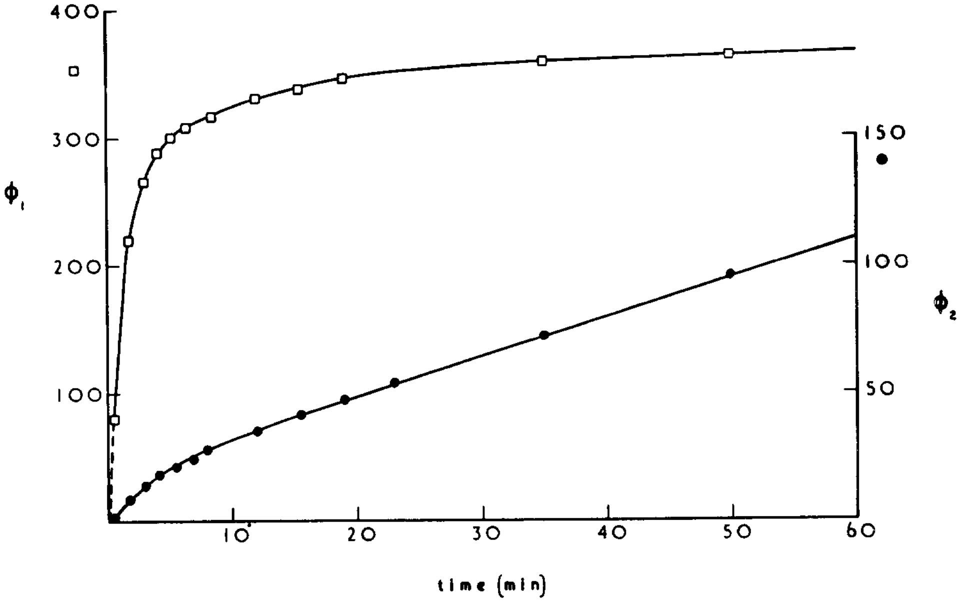


FIG. 3. Exchange of 1,1,3,3-tetramethylcyclopentane (I) on rhodium at 31°C: □, $\phi_1 = \Sigma_1^4\, id_i'$; ●, $\phi_2 = \Sigma_5^{15}\, id_i$.

Values of M, the mean number of deuterium atoms entering each molecule initially, are given in Table 2 and there was good agreement between values determined from the initial distributions or from Eq. (3). This was true for the other compounds as well and so only a single value of M is quoted for them. Two types of distributions of products were observed for compound I. Palladium and platinum at low temperatures gave only the d_1 and d_2 isomers but nickel and rhodium gave also d_3 and d_4. The maxima occurred at d_1 and d_4 for nickel but at d_2 and d_4 for rhodium. Increase of temperature enhanced d_2 in comparison with d_1, and d_3 plus d_4 in comparison with d_1 plus d_2 over rhodium. A second effect of increasing the temperature from 0° to 30°C was the exchange of a further three hydrogen atoms on platinum (products up to $d_5 = 2 + 3$) and rhodium (products up to $d_7 = 4 + 3$). This effect

Rhodium and platinum catalyzed the exchange of I at 0°C with initial rates (%/min 10 mg) of 59 and 0.8, respectively. A rate of 0.16 [using 100 cm^2 of catalyst surface as standard (*14*)] was obtained on palladium at 75°C but nickel was only active above 100°C (0.5 at 145°C). Good linear plots of ϕ against time, Eq. (2), were found for the slow reactions on platinum and palladium and a satisfactory ϕ-plot, Eq. (1), assuming that ϕ_∞ is 350 corresponding to four exchangeable hydrogen atoms, was obtained on platinum at 30°C and is shown in Fig. 4. The corresponding ϕ-plot for rhodium at 0°C was curved and indicated that the reaction was slowing down due to self-poisoning of the reactant-catalyst system. Self-poisoning also occurred on nickel at 145°C because a second reaction mixture gave a rate only ⅕th of that for the first mixture although the distribution of products and the value of M

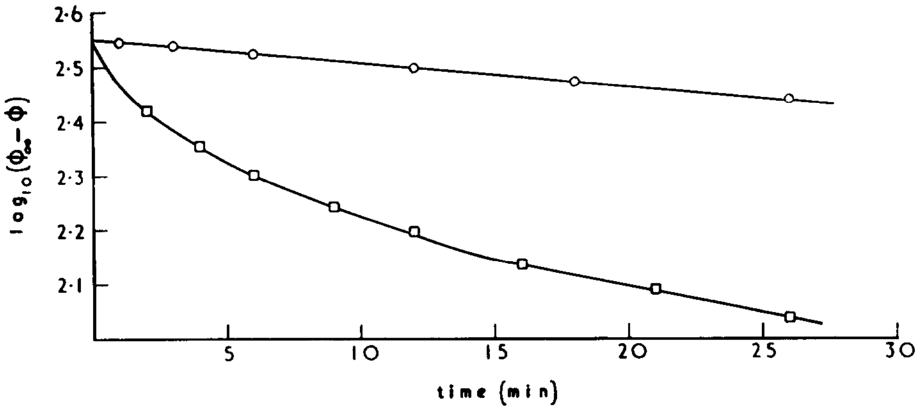


FIG. 4. ϕ-Plots (Eq. 1) for the exchange of 1,1,3,3-tetramethylcyclopentane: ○, platinum at 30°C; □, rhodium at 0°C.

were unchanged and gas-chromatographic analysis showed that no cracking had taken place.

Compound II—1,1,3,3,4-Pentamethylcyclopentane

The initial distributions shown in Table 3 indicate that over palladium and over nickel at high temperatures six hydrogen atoms, those on carbon atoms 4, 5, and 6, are exchanged in a single sojourn of the molecule on the surface of the catalyst. At 0°C maxima were obtained at d_2 and d_5 for rhodium but the first of these was not observed at 33°C and at this higher temperature d_6 had increased substantially, indicating that a reaction mechanism similar to those over palladium and nickel was operating. The appearance of isomers up to d_9 with platinum and rhodium at the higher temperatures showed that, as with compound I, some exchange of hydrogen atoms in the *gem*-dimethyl groups was occurring.

The order of activity of the metals was similar to that for compound I. Rates of 22, 65, and 0.7 %/min 10 mg were obtained on rhodium, platinum, and nickel at 0°, 50°, and 175°C, respectively, and k_{II} on palladium at 80°C was 0.7 %/min 100 cm^2. The increase of ϕ with time was linear for palladium at 80°C but curved for nickel at 175° because of self-poisoning.

TABLE 3
INITIAL AND OTHER DISTRIBUTIONS OF PRODUCTS FOR THE ECXHANGE OF 1,1,3,3,4-PENTAMETHYLCYCLOPENTANE (II)

Catalyst Temp. (°C)	Pt 0°	Pt 50°	Pd 80°	Ni 175°	Rh 0°	Rh[a] 33°	Rh[b] 33°
d_1	78	64	54.7	59	3.8	7.2	4.0
d_2	20	30.8	1.5	5.2	37	5.2	7.4
d_3	2	3.0	<1	3.1	13.0	5.6	9.5
d_4	—	1.1	<1	0.7	13.3	9.7	18.5
d_5	—	0.6	4.4	0.9	32	54.9	40.7
d_6	—	0.3	39.4	31.1	0.9	16.0	15.2
d_7	—	0.1	<1	<1	<0.2	0.8	2.9
d_8	—	0.07	—	—	—	0.4	1.5
d_9	—	0.03	—	—	—	0.2	0.3
M	1.2	1.45	3.1	2.65	3.35	4.54	—

[a] Distribution at t = 1.0 min (d_0 = 58.3%).
[b] Distribution when d_0 had decreased to 10%.

Compound III—trans-1,1,3,4-Tetramethylcyclopentane

Distributions, Table 4, showed a pronounced maximum at d_{12} for palladium, corresponding to the exchange of twelve hydrogen atoms on carbon atoms number 2 to 7, with subsidiary maxima at d_1 and d_5. Maxima at d_{12} were also obtained with nickel at 78°C and to a lesser extent with platinum at 50°C but at low temperatures these metals only produced initially isomers up to d_5. All the hydrogen atoms in the molecule were exchangeable on platinum at 50° because there were appreciable concentrations of the d_{13}, d_{14}, and d_{15} isomers formed initially (as the analyses were carried out on the pseudoparent ions C_8X_{15}, species with more than fifteen deuterium atoms could not be observed).

Fresh films of rhodium were too active at 0°C to permit the determination of initial distributions and so the catalyst was partly poisoned either by carrying out one run with consequent self-poisoning or by inclusion of oxygen (as air) in the reaction mixture before distributions were measured. Five hydrogen atoms were exchangeable initially on rhodium but there was a pronounced maximum at d_2 and a smaller maximum at d_4. The course of the exchange reaction on this metal at 0°C, last column of Table 4 and Fig. 5, showed that the 18 hydrogen atoms in the molecule could be classified in groups of 4,3,3,2, and 6 in decreasing ease of exchange.

In contrast to the results with compounds I and II, nickel was active for the exchange of III at 0° and the activities of the other three metals were also slightly greater. Rates at 0°C of 114, 19.5, and 1.9 %/min 10 mg were found for rhodium, nickel, and platinum, respectively, and 3%/min 100 cm² for palladium at 95°C. Possible reasons for the different order of activity of the metals with compound III will be given in the next section.

TABLE 4
INITIAL AND OTHER DISTRIBUTIONS OF PRODUCTS FOR THE EXCHANGE OF TRANS-1,1,3,4-TETRAMETHYLCYCLOPENTANE (III)

Catalyst	Pt[a]	Pt	Pd	Pd	Ni	Ni[b]	Rh[c]	Rh[d]	Rh[e]
Temp. (°C)	0°	50°	80°	95°	0°	78°	0°	24°	0°
d_1	58.4	40.5	8.1	10.7	73.5	15.6	13.4	16.3	4.1
d_2	31.4	27.5	1.8	1.4	22.0	34.3	56.6	55.8	13.7
d_3	5.9	11.0	1.1	0.3	2.2	8.0	8.5	10.1	23.8
d_4	2.6	4.5	1.8	0.5	1.5	6.0	18.7	12.4	43.9
d_5	1.7	2.9	6.6	1.9	0.7	4.2	2.8	4.5	6.0
d_6	<1.0	1.6	0.2	<0.5	0.1	2.2	<1.0	0.9	4.2
d_7	—	1.2	0.4	—	<0.1	1.6	<0.5	<0.2	4.0
d_8	—	0.8	0.5	—	—	1.2		—	0.1
d_9	—	0.4	0.8	—	—	1.6	<0.1	—	0.1
d_{10}	—	0.6	1.1	1.1	—	3.0	—	—	0.1
d_{11}	—	1.1	9.6	8.9	—	6.7	—	—	—
d_{12}	—	3.4	66.9	75.2	—	15.6	—	—	—
d_{13}	—	2.1	1.1	<2.0	—	<1.0	—	—	—
d_{14}	—	1.6	—	—	—	—	—	—	—
d_{15}	—	0.8	—	—	—	—	—	—	—
M	1.58	3.1	10.1	10.4	1.34	4.96	2.14	2.36	—

[a] Distribution at t = 1.0 min (d_0 = 97.7%).

[b] After a first run at 50°C for 30 min.

[c] After a first run at 0°C for 50 min, distribution at t = 2.0 min (d_0 = 65.0%).

[d] With 8% air in the reaction mixture.

[e] Distribution when d_0 had decreased to 10%.

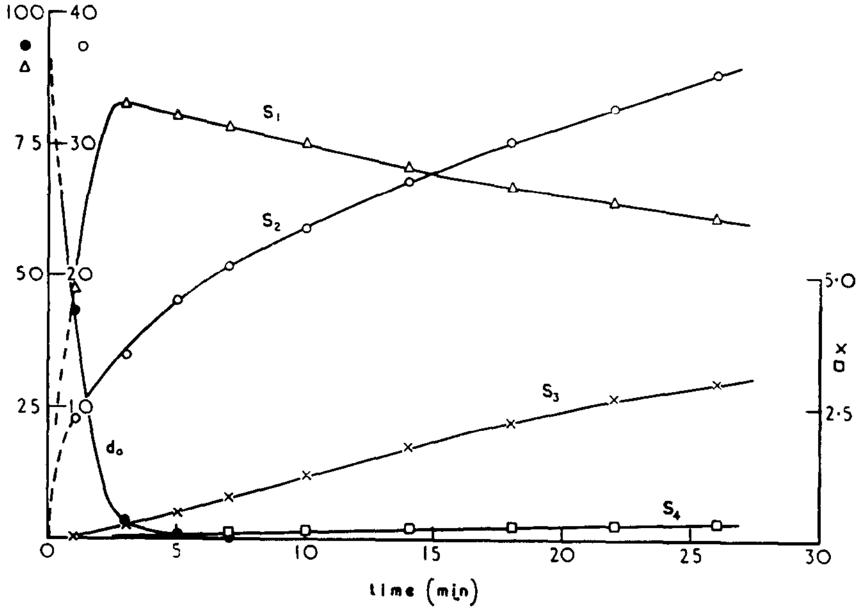


FIG. 5. Exchange of *trans*-1,1,3,4-tetramethylcyclopentane on rhodium at 0°C: ●, d_0; △, $S_1 = \Sigma_1^4 d_n$; ○, $S_2 = \Sigma_5^7 d_n$; ×, $S_3 = \Sigma_8^{10} d_n$; □, $S_4 = d_{11} + d_{12}$.

Compound IV—cis-1,1,3,4-Tetramethylcyclopentane

The interesting feature of the distributions in Table 5 is that a maximum was always observed at the d_{12} isomer on all the metals. This maximum was very small on rhodium and on nickel at 0°C, of moderate size on nickel at 43° or on platinum at 26° or 50°, and very large on palladium at all temperatures. The twelve hydrogens readily exchangeable on palladium were those on carbon atoms numbers 2 to 7. One distribution obtained from the exchange of compound VII on palladium is given in Table 5 in order to show that this compound was not present in sufficiently substantial quantity as an impurity in IV to influence the other distributions in Table 5 significantly. Two effects were caused by increase of temperature on palladium—the development of a maximum at d_1 and at 146° the exchange of hydrogen atoms in the *gem*-dimethyl group; the latter also occurred to an appreciable extent on platinum even at 26°C. Ten hydrogen atoms were readily exchanged initially on rhodium at 0°C and subsidiary maxima at d_2, d_4, and d_7 (very small) were observed.

Considerably different rates of reaction were found for the two samples IV and IV* on palladium—values of 1.2 at 80°C and 4%/min 100 cm² at 60°C, respectively. Sample IV* reacted on nickel at 0°C (0.36 %/min 10 mg) but no reaction occurred with sample IV at this temperature. If we accept the hypothesis that traces of oxygen-containing compounds poison nickel strongly, it seems clear that I, II and IV contain such impurities whereas III and IV* do not and this is in accord with expectation based on their method of preparation. Rates of 210 and 4 %/min 10 mg were obtained with sample IV on rhodium at 0°C and on platinum at 26°C, respectively.

Other Compounds

The initial distribution for the exchange of 1,1,2,4-tetramethylcyclopentane (VII) on palladium at 42°C given in Table 5 showed a pronounced maximum at the d_{12} isomer with additional maxima at d_7 and d_{10}. The distributions obtained with *cis*-1,2-dimethylcyclopentane (V) and 1,1,3-trimethylcyclopentane (VI) over palladium (Table 6) were similar to those from com-

TABLE 5

INITIAL DISTRIBUTION OF PRODUCTS FOR THE EXCHANGE OF *cis*-1,1,3,4-TETRAMETHYLCYCLOPENTANE (IV) AND ONE DISTRIBUTION ON PALLADIUM FOR 1,1,2,4-TETRAMETHYLCYCLOPENTANE (VII)

Catalyst Temp. (°C)	Pt 26°	Pt[a] 50°	Pd 40°	Pd 87.5°	Pd 146°	Pd[b] 42°	Ni[a] 0°	Ni 43°	Rh[c] 0°
d_1	20.5	16.2	<2	6.5	18.6	<0.2	77.6	25.0	3.0
d_2	8.0	7.7	<2	<0.5	1.0	<0.2	17.0	23.5	13.5
d_3	4.0	3.7	<1	<0.5	<0.4	<0.2	2.4	5.0	7.9
d_4	3.7	3.3	<1	<0.5	<0.4	<0.2	1.6	4.7	10.3
d_5	3.4	3.1	<1	<0.5	<0.4	<0.2	<1.0	3.7	6.8
d_6	2.3	2.8	<1	<0.7	<0.4	3.1	<0.7	3.1	7.4
d_7	2.4	3.2	<1	<0.7	<0.4	12.3	<0.7	3.0	7.5
d_8	2.9	3.5	<1	<0.7	<0.4	1.8	<0.5	3.1	6.6
d_9	3.5	3.7	<1	<0.7	<0.4	7.3	<0.5	4.0	14.2
d_{10}	4.6	5.1	<2	1.2	1.3	20.9	<0.5	6.9	21.2
d_{11}	7.0	7.1	7.5	7.3	8.8	7.6	0.6	7.1	0.5
d_{12}	25.1	21.2	92.5	84.8	62.4	47.0	0.8	10.9	1.1
d_{13}	7.0	9.7	<0.5	0.2	6.7	<0.2	—	<0.5	<0.1
d_{14}	3.0	6.4	—	—	1.2	—	—	—	—
d_{15}	2.6	3.3	—	—	<0.3	—	—	—	—
M	7.62	8.2	11.9	11.2	9.8	10.4	1.4	5.03	6.37

[a] Experiments with IV*.

[b] Distribution for VII.

[c] Distribution at $t = 0.5$ min ($d_0 = 69\%$).

TABLE 6

SOME INITIAL DISTRIBUTIONS OF PRODUCTS FOR THE EXCHANGE OF OTHER HYDROCARBONS.

Compound Catalyst Temp. (°C)	V Pd 26°	*cyclo*-C_6H_{10} [a] Pd 25°	VI Pd 70°	VIII Rh 16°
d_1	<0.5	18.2	2.4	9.8
d_2	<0.2	9.6	1.4	12.9
d_3	<0.2	3.8	<0.3	9.6
d_4	<0.2	5.3	<0.3	10.9
d_5	<0.2	17.7	<0.3	6.9
d_6	<0.2	0.3	1.0	4.8
d_7	<0.2	0.8	4.8	6.3
d_8	<0.2	5.8	0.2	5.4
d_9	<0.2	6.2	8.2	4.8
d_{10}	2.0	32.3	82.0	8.1
d_{11}	18.0	—	—	20.5
d_{12}	<0.7	—	—	—
d_{13}	14	—	—	—
d_{14}	66	—	—	—

[a] Results taken from Anderson and Kemball (*10*).

pounds III, IV, and VII in that the main isomer obtained was the one corresponding to the replacement of all hydrogen atoms apart from those in the *gem*-dimethyl group. Small maxima at d_{11} and d_7 were also observed for V and VI, respectively. The initial distribution shown in Table 6 for the exchange of 2,3-dimethylbutane (analyzed by the pseudoparent ions $C_5X_{11}^+$) on rhodium was very similar to that for compound IV (Table 5) with a marked maximum at d_{11} and subsidiary maxima at d_2, d_4, and d_7.

Kinetics of cis-trans Isomerization in Conjunction with Exchange

The rate constant k_H for the disappearance of the light isomer is defined by the equation

$$-\frac{d(d_0)}{dt} = k_H \frac{(d_0) - (d_0)_\infty}{100 - (d_0)_\infty} \quad (4)$$

in which (d_0) is the percentage of the light isomer present at time t and $(d_0)_\infty$ is the equilibrium value which was negligible with the reaction mixtures used. We may define a rate constant k_I for the isomerization of a *cis*-1,2-dimethylcyclopentane to the corresponding *trans*-isomer by an analogous equation

$$-\frac{dx}{dt} = k_I \frac{x - x_\infty}{100 - x_\infty} \quad (5)$$

in which x represents the percentage of the *cis*-isomer present at time t and x_∞ in the equilibrium value. Integration of (4) and (5) and elimination of t leads to the equation

$$\log \frac{x - x_\infty}{x_0 - x_\infty} = \frac{k_I}{k_H} \frac{100}{100 - x_\infty} \log \frac{(d_0)}{100} \quad (6)$$

where x_0 is the percentage of the *cis*-isomer present at $t = 0$. Thus, a single determination of x and (d_0) for a hydrocarbon which has reacted for a given time is sufficient to determine the ratio k_I/k_H if the equilibrium percentage x_∞ is known.

For experiments in which the original hydrocarbon is the *trans*-isomer, an equation analogous to Eq. (6) can be used to determine k_I'/k_H.

Most of the experiments on *cis-trans* isomerization were carried out with compound IV because the equilibrium favors the *trans*-isomer and consequently it is easier to follow the conversion of *cis* to *trans* than the reverse reaction. Table 7 records a series of corresponding measurements of x and (d_0) obtained with sample IV* on palladium at 65°C. These were used to test Eq. (6) by plotting log $(x—x_\infty)$ against log (d_0) as shown in Fig. 6, using a value of x_∞ of 15% which was the approximate equilibrium percentage indicated by a number of experiments. It is clear that while there is a good correlation between the extents of isomerization and exchange, Eq. (6) does not hold accurately, as the line in Fig. 6 shows some curvature. One reason for this may be that Eq. (4) is not strictly obeyed in exchange reactions and does not have the same validity as Eq. (5) or as Eq. (1). Furthermore, any self-poisoning which may occur during reaction may interfere with exchange and isomerization to different extents. The linear portion of the plot in Fig. 6 gives a value of 0.51 for k_I/k_H, i.e., one of every two molecules undergoing exchange is isomerized to the *trans*-isomer. Similar values of the ratio were obtained for reactions on palladium at other temperatures such as 87° or 146°. The ratio was zero for reactions on rhodium at −21° or 95°C and temperature-dependent on platinum rising from 0.10 to 0.15 between 26° and 50°C and on nickel rising from zero at 0°C to 0.19 at 43°C.

A few experiments with compound III showed that the ratio k_I'/k_H varied in a similar manner from metal to metal although the values were much smaller than those for k_I/k_H. The results are given in Fig. 7 which shows that the ratio of isomerization (in either direction) to exchange

TABLE 7

COMPARISON OF THE PERCENTAGE x OF *cis*-ISOMER WITH THE PERCENTAGE OF d_0 REMAINING FOR THE EXCHANGE OF *cis*-1,1,3,4-TETRAMETHYLCYCLOPENTANE (SAMPLE IV*) ON PALLADIUM AT 65°C

d_0	100	82.0	50.3	49.9	27.6	19.5	13.7
cis-isomer	98	95	81	82	62	50	45

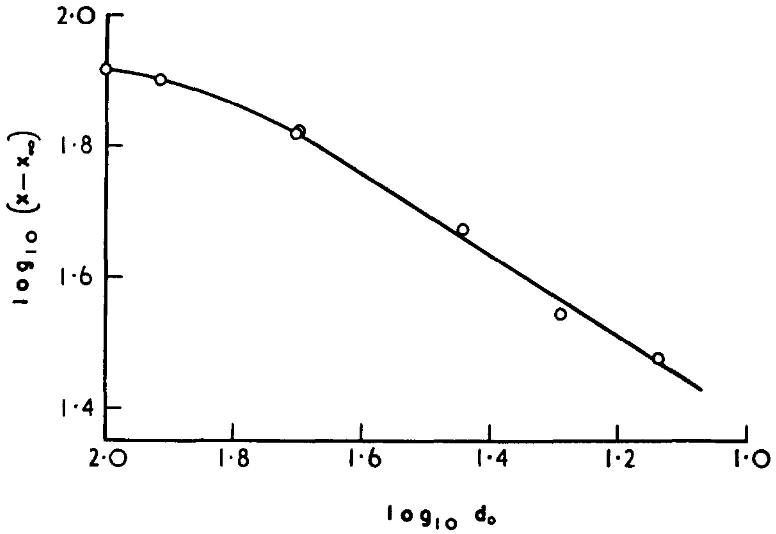


FIG. 6. The relationship between exchange and isomerization of *cis*-1,1,3,4-tetramethylcyclopentane (IV) on palladium; plot to test Eq. (6).

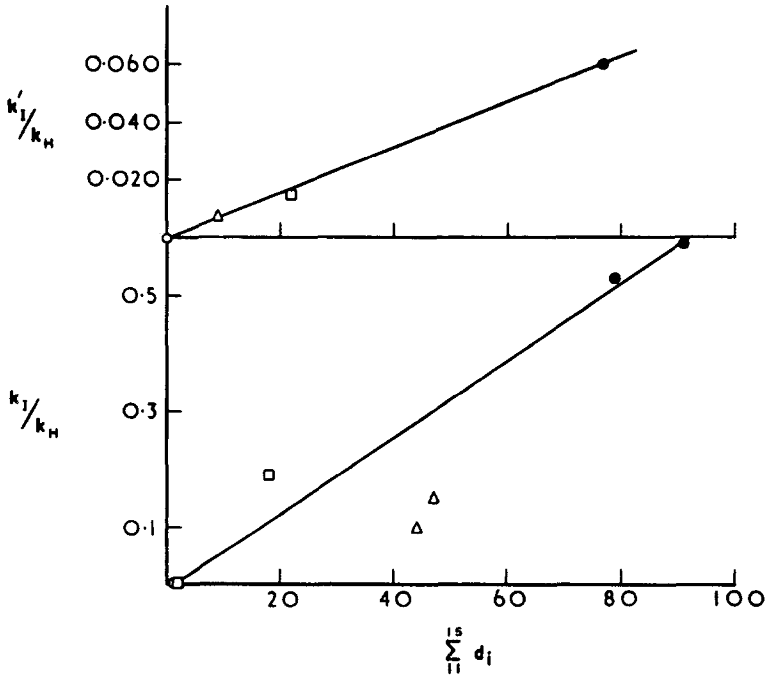


FIG. 7. The correlation of the ratio of isomerization to exchange with the initial production of isomers in the range d_{11} to d_{15}. Upper section, k_I'/k_H for compound III; ○, rhodium at 0°C; △, platinum at 50°C; □, nickel at 78°C; and ●, palladium at 80°C. Lower section, k_I/k_H for compound IV; the symbols refer to the same metals as in the upper section and other details are given in the text.

is approximately related to the production of the isomers above d_{10} in the initial stage of the exchange reactions. The ratios are high on palladium, very low on rhodium, and the other two metals show temperature-dependent intermediate values.

Isomerization occurred with compound V in a similar manner to the reaction with IV; on palladium at 50°C, 10% and 58% of the *trans*-isomer were formed when 41% and 88%, respectively, of the d_0 isomer had disappeared.

DISCUSSION

Cis-trans Isomerization

The occurrence of *cis-trans* isomerization with compounds III, IV, and V implies the presence of an intermediate in which the relevant methyl groups are brought into the plane of the rings and we believe such intermediates are π-bonded to the surface. The results in Table 7 and Fig. 6 for the reaction of IV on palladium show that isomerization and exchange are closely related and the correlation in Fig. 7 suggests that the intermediate responsible for isomerization is also producing isomers above d_{10} in the exchange process which supports the hypothesis that it is π-bonded to the surface.

The ratio of isomerization to exchange is always high on palladium because π-bonded intermediates are formed in the same temperature range as the σ-bonded, α or αβ species. It seems clear that π-bonded intermediates are formed on the other three metals at similar temperatures to those for palladium, i.e., above 40°C for compound IV. The factor causing the differences in the ratio of isomerization to exchange from metal to metal is the relative ease of formation of σ-bonded and π-bonded species on each metal. Rhodium is exceptionally active for catalysis by σ-bonded species and so the extent of isomerization is small compared with the rate of exchange at all temperatures although isomerization does occur around 90°C with compound IV. With platinum and nickel, rise of temperature increases the proportion of π-bonded to σ-bonded species with a consequential rise in the ratio of isomerization to exchange.

Our results provide an interpretation of the observations made by Sauvage, Baker, and Hussey (*20*) on the hydrogenation of several disubstituted cycloalkenes. They found that more isomeric cycloalkenes and more *trans*-cycloalkanes were formed on palladium than on platinum. Both these results can be explained by the predominance of π-bonded intermediates on palladium in contrast to the greater part played by σ-bonded species on platinum leading to the production of *cis*-cycloalkanes.

Palladium

The results of all the exchange reactions provide excellent support for the theory that π-bonded intermediates can be formed provided molecules have three or more adjacent nonquaternary carbon atoms. Compound I, with only two such atoms, does not form the π-bonded intermediate and the initial exchange is limited to a pair of hydrogen atoms on one side of the ring. Similar results were obtained by Burwell, Shim, and Rowlinson (*11*) for the exchange of *nor*-bornane on palladium supported on γ-alumina because the geometry of the molecule will not permit the formation of a 3-carbon π-bonded species. The absence of d_3 and d_4 isomers in the initial distributions from I show that the propagation of exchange either by αα-diadsorbed species or the species postulated by Burwell and his colleagues (*11*) does not take place on palladium.

The additional methyl group in II permits the π-bonded intermediate to form with the expected initial formation of the d_8 isomer. Furthermore, with all the compounds from III to VII the most abundant initial product corresponds to the replacement of all hydrogen atoms except those in *gem*-dimethyl groups because all have the required structure to form π-bonded intermediates. If αα-diadsorbed intermediates were important on palladium, III should give a maximum at the d_6 isomer but this was not found. Most of the subsidiary maxima observed with palladium, e.g., d_5 for III, d_{11} for V, d_7 for VI, and d_{10} for VII, can be explained by the completion of the exchange of groups of hydrogen atoms by an $\alpha\beta$ process (see Table 1). The only anomaly is the maximum at d_7 for VII. We believe, on the basis of the greater ease of exchange of IV than III, that the *cis* isomer in compound VII will exchange more rapidly than the *trans* and hence determine the main features of the initial distribution such as the maximum at d_{10}. The unexpected maximum at d_7 may be explained by some steric hindrance associated with the replacement of the hydrogen atoms in the methyl group (carbon atom number 2) adjacent to the *gem*-dimethyl group.

The rise in the maximum at d_1 for IV (Table 5) with increase of temperature is probably due to exchange of one of the hydrogen atoms in the *gem*-dimethyl group by a monoadsorbed intermediate [cf. exchange of neopentane (*8*)]. Likewise, the initial formation of d_{13}, d_{14}, and d_{15} in small amounts at the comparatively high reaction temperature of 146°C must be attributed to repeated exchange of the hydrogen atoms on the methyl group nearer the catalyst while the bulk of the molecule is held as a π-bonded complex, i.e., involving a $\sigma(8)$-$\pi(2,3,4,5)$ complex (cf. Fig. 2). It is unlikely (*8*) that σ-bonded $\alpha\gamma$-diadsorbed intermediates are important on palladium at 146°C.

We believe that the two differences between the results for V and those obtained earlier (*10*) for cyclopentane (Table 6), i.e., the higher ratio of $d_{14}:d_{11}$ than for $d_{10}:d_5$ and the almost complete absence of light isomers from the dimethyl compound are significant and attributable to the effect of the methyl substituents on the ring. These will, by virtue of hyperconjugation, influence the delocalization energy of the π-electron systems and favor the formation of π-bonded as opposed to σ-bonded intermediates. This factor will be even more important in the polymethylcyclopentanes. The interconversion between 3-carbon and 4-carbon π-bonded species is probably more rapid than the interconversion between σ-bonded and π-bonded species because the former only involves an extension but the latter an initiation of sp^2 hybridization.

The position as well as the number of the methyl substituents may influence the ease of formation of π-bonded intermediates. Thus, IV with adjacent methyl groups gives a larger amount of the d_{12} isomer initially than VII with isolated methyl substituents and correspondingly less of lower isomers (Table 5). It seems that the inductive and hyperconjugative effects are enhanced when the methyl groups are on adjacent carbon atoms with a consequent increase in the part played by π-bonded compared with σ-bonded intermediates in the exchange process. Effects of substituent groups of this kind may have a widespread importance for many reactions on metal catalysts in relation to selectivity and the rates of reaction of different isomeric compounds. A good example is the relative rates of hydrogenation of various substituted benzenes. These compounds can readily adsorb as π-complexes and the ease of hydrogenation will decrease with the stability of the complexes and hence the number of methyl substituents as found in practice (*21*). Again, the position of the substituents is important and *ortho*-xylene with adjacent methyl groups is less easily hydrogenated than the other xylenes (*22*).

Platinum

The initial distributions for I, II, and III on platinum at 0°C show no isomers beyond the first group of hydrogen atoms exchangeable by the operation of an $\alpha\beta$ process. In fact, there is a tendency not to complete the exchange of methyl groups in this first group of atoms as shown by the cutoff in the distribution after d_2 for both II and III instead of after d_5 as expected from Table 1.

The extension of the distributions at higher temperatures to include with I and II an additional three or six isomers, respectively, clearly involves the exchange of hydrogen atoms in *gem*-dimethyl groups by σ-bonded $\alpha\gamma$-intermediates. The exchange of neopentane on platinum was not investigated by Kemball (*8*) but the ability of this metal to form $\alpha\gamma$-species may be significant in explaining its unique behavior in forming *n*-butane in the cracking of neopentane, which was discovered by Anderson and Baker (*23*).

The production of d_{11} and d_{12} isomers from III at 50° and from IV even at 26°C (Tables 4 and 5) shows that π-bonded intermediates are formed on platinum as on palladium but the relatively lower importance of the π-bonded species to the σ-bonded intermediates on platinum is obvious from a comparison of the distributions on the two metals. The results with both compounds at 50°C provide further evidence of the high activity of platinum for the exchange of hydrogen atoms in *gem*-dimethyl groups and for the importance of $(\sigma + \pi)$-bonded intermediates as postulated for IV at 146°C on palladium.

Nickel

We have already suggested that the need for temperatures above 100°C to exchange I and II on nickel may not be a genuine effect but a consequence of the presence of oxygen-containing impurities. The chief new feature with nickel is the substantial initial production of the d_4 isomer from I at 144°C which contrasts with the results on palladium and platinum. We believe that exchange is propagating from one side of the cyclopentane ring to the other side by $\alpha\alpha$-diadsorbed intermediates and it is worth noting that nickel and rhodium were the most active metals for the exchange of methane (*7*) by the mechanism involving adsorbed methylene radicals ($\alpha\alpha$-diadsorbed methane).

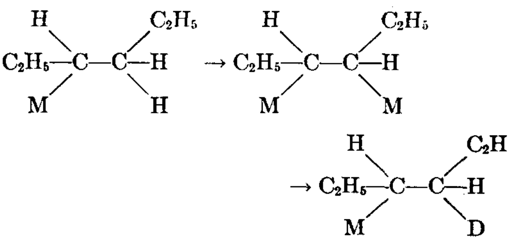
The results with III and IV showed a similar behavior to those obtained on platinum in that exchange by σ-bonded intermediates predominated at low temperatures but there was increasing participation of π-bonded species at higher temperatures. The pattern for II at 175°C on nickel was almost identical to that found on palladium at 80°C.

Rhodium

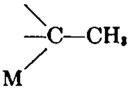
The formation of d_3 and d_4 isomers from I on rhodium at 0°C shows that rhodium, like nickel, can form $\alpha\alpha$-diadsorbed intermediates. More of these isomers are produced at 30° because there is a higher activation energy required for $\alpha\alpha$ than for the ordinary $\alpha\beta$-adsorbed species in agreement with the results for the exchange of methane (*7*).

Our observations on self-poisoning of the exchange reactions, which was greatest on rhodium and on nickel, confirm the hypothesis put forward by Gault and Kemball (*19*) that metals which form $\alpha\alpha$-diadsorbed species can also form $\alpha\alpha\beta$ and $\alpha\alpha\beta\beta$ species are therefore more susceptible to self-poisoning.

Rhodium is the most active of the metals studied for the exchange of all the compounds and rather complex patterns of products are formed initially because of the extreme rapidity of $\alpha\beta$ exchange processes. The first anomalous feature is the presence of a maximum at d_2 for compounds II, III, IV, and VIII which tends to be more pronounced at lower temperatures. This behavior has been observed previously for the exchange of isobutane (*5*) and for *n*-pentane and *n*-hexane (*19*). Again, maxima at d_4 are found with most of the compounds (III, IV, and VIII) which contain the grouping $>$CH.CH$_3$ and this was noticeable with isobutane (*5*) as well. We believe that these arise because rotational processes of species on the catalyst surface are slower than the exchange by $\alpha\beta$ adsorbed species with a consequential subdivision of the groups of hydrogen atoms normally (e.g., on palladium) exchangeable by $\alpha\beta$ processes. This hypothesis can be illustrated by the following adsorbed species from *n*-hexane:



If the rotation of the group C$_3$H$_6$D in the alkyl species on the right-hand side is slow, the species may be desorbed as a d_2 isomer before additional hydrogen atoms are replaced by further α to $\alpha\beta$ interconversion. Similar restrictions will apply to the exchange of any of the hydrogen atoms in the ethyl group attached to the adsorbed carbon atom because this would necessitate rotation of the whole molecule around the bond to the metal atom. On the other hand, the rotation of a methyl group in a species of the type



would be less hindered and, therefore more rapid, so that the likely product would be the compound $>CD-CD_3$, i.e., a d_4 isomer. This explanation is in agreement with the observations and it is also supported by the absence of any maximum at the d_2 isomer for the exchange of ethane on rhodium (*3*).

We can now discuss the way in which the hydrogen atoms in compound III divide into groups of increasing difficulty of exchange on rhodium. The pair of hydrogen atoms on carbon atoms 2 and 3 on the same side of the ring and the corresponding pair on carbon atoms 4 and 5 are the most easily exchanged. The hydrogen atoms in the methyl group on carbon atom 3 are associated with the first pair of hydrogen atoms and make up the group of five atoms (Table 1) exchangeable in a single $\alpha\beta$ process on palladium; similarly, those in the methyl group on carbon atom 4 are associated with the second pair. The formation of the d_5 to d_7 isomers on rhodium is due to the exchange of the easy four and one methyl group; and the d_8 to d_{10} isomers correspond to the four with both methyl groups. At each adsorption of the molecule, the exchange process may propagate to only one of these methyl groups and consequently the buildup of the d_8 to d_{10} isomers follows the buildup of the d_5 to d_7. The last two hydrogen atoms to be exchanged are those on carbon atoms 2 and 5 situated between methyl groups and so sterically hindered and at 0°C the six atoms in the *gem*-dimethyl group are not replaced.

At higher temperatures, e.g., around 30°C, rhodium is active for exchange involving $\alpha\gamma$ species as shown by the pattern of products obtained initially from I and II and as expected from the behavior of neopentane on this metal (*8*). However, π-bonded species play little or no part in determining the initial distributions because the reactions of the σ-bonded intermediates is so rapid. The trace of d_{11} and d_{12} formed from IV at 0° must be due to $\alpha\alpha$-diadsorbed species and not to π-bonded species because there was negligible isomerization at this temperature.

Some General Points

Important conclusions follow from the belief that π-bonded species are adsorbed on individual metal atoms. Noncyclic molecules must adopt a semicyclic configuration before forming π-bonded intermediates, i.e., 1,3-dienes are expected to adsorb in the *syn*-configuration and to give, on hydrogenation, preferentially *cis*-monoolefins. The comparatively rapid isomerization between *cis*-but-2-ene and but-1-ene observed by Hamilton and Burwell (*12*) may occur because these compounds can both form a common 3-carbon or 4-carbon π-bonded species. On the other hand, *trans*-but-2-ene can only form a 3-carbon complex and this would only be convertible into the first type of complex through σ-bonded intermediates. The postulate that isomerization of olefins can occur through π-bonded species is supported by the higher temperature coefficient for isomerization than hydrogenation reported by Taylor (*24*) and may well avoid the difficulties emphasized by Hamilton and Burwell in explaining the kinetics of isomerization by means of mono- and diadsorbed intermediates.

We believe these geometrical considerations can explain the behavior observed in the deuteration of 4-methylmethylenecyclohexane on iron films by Erkelens, Galwey, and Kemball (*13*). This molecule with the double bond in the exocyclic position can only form a 3-carbon π-bonded complex and the double-bond migration into the ring and the formation of ring π-bonded complexes via σ-bonded intermediates is necessary before extensive exchange of the ring is possible during deuteration. Under these circumstances, it is not surprising that the molecule behaved more like ethylene than cyclohexene at lower temperatures and only showed extensive exchange of the ring at higher temperatures.

The ability of unsintered iron films to form π-bonded species indicates that there must be metal atoms present with the required orbitals vacant or with the appropriate symmetry for bonding. Such atoms may be in a metastable state as they will be less firmly bonded to the bulk of the metal and it is not surprising that sintering the films causes a considerable reduction in the number of sites suitable for the formation of adsorbed π-bonded intermediates. The formation of ferrocene by the passage of cyclopentadiene (*25*) over an iron catalyst is clearly a special case of the removal of active metal atoms by π-complexing.

A possible advantage of highly dispersed but supported metal catalysts may be the presence even after sintering of sufficient metal atoms suitable for π-bond formation. The observation by Pitkethly and Goble (*26*) that each platinum atom on a platinum-alumina catalyst can adsorb an average of 0.72 molecules of benzene provides excellent support for our suggestion that only a single metal atom is required to form an adsorbed π-bonded complex.

The introduction of the concept of π-bonding in heterogeneous catalysis has considerable advantages. It is generally applicable and provides an important link between catalytic behavior in a great many reactions and the chemistry of the transition elements. Recent work by Burwell *et al.* (*27*) with chromium oxide catalysts shows that the concepts of π-bonding are also valuable in explaining reactions on the oxides of transition metals. They found that complex exchange could occur with any hydrocarbon capable of forming an allylic radical, i.e., having three or more adjacent nonquaternary carbon atoms.

The concept may also provide explanations of the reactions of acetylenic compounds which may give strong π-bonding involving both the π_y and π_z electrons and suitably oriented metallic orbitals. It is significant that the polymerization of acetylene is catalyzed by solid metals and also by metallic complexes in homogeneous solutions where π-bonding is known to operate.

ACKNOWLEDGMENTS

One of us (J.J.R.) is an I.C.I. Research Fellow, and another (C.K.) wishes to thank the Department of Scientific and Industrial Research for a grant to purchase the MS. 2 mass spectrometer.

REFERENCES

1. KEMBALL, C., *Advances in Catalysis* **11,** 223 (1959).

2. KEMBALL, C., *Proc. Chem. Soc.* p. **264** (1960).

3. ANDERSON, J. R., AND KEMBALL, C., *Proc. Roy. Soc.* **A223,** 361 (1954).

4. ROWLINSON, H. C., BURWELL, R. L., JR., AND TUXWORTH, R. H., *J. Phys. Chem.* **59,** 225 (1955).

5. KEMBALL, C., *Proc. Roy. Soc.* **A223, 377** (1954).

6. ADDY, J., AND BOND, G. C., *Trans. Faraday Soc.* **53,** 368, 383, 388 (1957).

7. KEMBALL, C., *Proc. Roy. Soc.* **A207,** 539 (1951); **A217,** 376 (1953).

8. KEMBALL, C., *Trans. Faraday Soc.* **50,** 1344 (1954).

9. BURWELL, R. L., JR., AND BRIGGS, W. S., *J. Am. Chem. Soc.* **74,** 5096 (1952).

10. ANDERSON, J. R., AND KEMBALL, C., *Proc. Roy. Soc.* **A226,** 472 (1954).

11. BURWELL, R. L., JR., SHIM, B. K. S., AND ROWLINSON, H. C., *J. Am. Chem. Soc.* **79,** 5142 (1957).

12. HAMILTON, W. M., AND BURWELL, R. L., JR., *Actes du Deuxième Congrès International de Catalyse,* Vol. I, p. 987. Éditions Technip, Paris, 1961.

13. ERKELENS, J., GALWEY, A. K., AND KEMBALL, C., *Proc. Roy. Soc.* **A260,** 273 (1961).

14. GAULT, F. G., AND KEMBALL, C., *Trans. Faraday Soc.* **57,** 1781 (1961).

15. ROONEY, J. J., GAULT, F. G., AND KEMBALL, C., *Proc. Chem. Soc.* p. 407 (1960).

16. MCCLELLAN, W. R., HOEHN, H. H., CRIPPS,

H. N., Muetterties, E. L., and Howk, B. W., *J. Am. Chem. Soc.* **83,** 1601 (1961).

17. Campbell, J. S., and Kemball, C., *Trans. Faraday Soc.* **57,** 869 (1961).

18. Kemball, C., *Proc. Roy. Soc.* **A210,** 413 (1952).

19. Gault, F. G., and Germain, J. E., *Bull. Soc. Chim. France* p. 1365 (1959).

20. Sauvage, J. F., Baker, R. H., and Hussey, A. S., *J. Am. Chem. Soc.* **83,** 3874 (1961).

21. Smith, H. A., *in* "Catalysis" (P. H. Emmett, ed.), Vol. V, p. 175. Reinhold, New York, 1957.

22. Smith, H. A., and Rader, C. P., *Actes du Deuxième Congrès International de Catalyse,* Vol. I, p. 1213. Éditions Technip, Paris, 1961.

23. Anderson, J. R., and Baker, B. G., *Nature* **187,** 937 (1960).

24. Taylor, T. I., *in* "Catalysis" (P. H. Emmett, ed.), Vol. V, p. 370. Reinhold, New York, 1957.

25. Millar, S. A., Tebboth, J. A., and Tremaine, J. F., *J. Chem. Soc.* p. 632 (1952).

26. Pitkethly, R. C., and Goble, A. G., *Actes du Deuxième Congrès International de Catalyse,* Vol. II, p. 1851. Éditions Technip, Paris, 1961.

27. Burwell, R. L., Jr., Littlewood, A. B., Cardew, M. H., Pass, G., and Stoddart, C. T. H., *J. Am. Chem. Soc.* **82,** 6272 (1960).