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Mechanism of Cyclopropane Hydrogenolysis on Metal Catalysts

III. Deuterolysis, Isomerization, and Cracking of Gemdialkylcyclopropanes[1]

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Deuterolysis, isomerization, and cracking of gemdimethyl- and gemdiethyl-cyclopropanes have been investigated on nine metal catalysts, namely, Pt, Pd, Rh, Ir, Fe, Co, Ni, and W, at −40 to +50°C and on Au at 375°C. On W and Au, the major reaction is an isomerization in which the ring breaks at the most substituted C–C bonds, followed in the case of W by very fast hydrogenation. On the other metals, hydrogenolysis takes place with ring cleavage at the bond opposite the substituted carbon atom. On Fe, Co, and Ni, it is accompanied by cracking, yielding methane and isobutane in the case of gemdimethylcyclopropane. The replacement of hydrogen by deuterium in the reaction mixture allows two mechanisms of hydrogenolysis to be distinguished. One, yielding $\alpha\gamma$-dideuteroalkanes, predominates on all metals: This is a simple addition of two deuterium atoms, presumably involving $\alpha\gamma$-diadsorbed species. The second mechanism, yielding trideutero- and tetradeuteroalkanes, is important on Pt and, to some extent, on Ir. A dissociatively adsorbed cyclopropyl radical is probably the precursor in this reaction, and this species may also play a role in hydrocracking.

INTRODUCTION

Hydrogenation of cyclopropane (*1*) is accompanied on some metals by two hydrocracking reactions (*2–6*):

$$C_3H_6 + H_2 \rightarrow C_3H_8$$

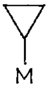
$$C_3H_6 + 2H_2 \rightarrow C_2H_6 + CH_4;$$

$$C_3H_6 + 3H_2 \rightarrow 3CH_4.$$

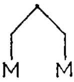
Three major problems concerning the mechanism are unsolved. These are: (a) the mode of adsorption of cyclopropane; (b) the nature of the rate-determining step; and (c) the relation between hydrogenation and hydrocracking of cyclopropane.

Adsorption of Cyclopropane

Three intermediate species have been proposed:



(A)



(B)

(C)

The adsorbed cyclopropyl intermediate (A), suggested first by Bond and Turkevich (*7*), seems to have been largely rejected because the exchange of cyclopropane with deuterium is negligible except in a few cases (*8, 9*). However, the self-hydrogenation of cyclopropane during chemisorption proves that such species exist (*4, 10, 11*). An $\alpha\gamma$-diadsorbed species B obtained from cyclopropane by simple ring cleavage is much more popular. The homogeneous analog of species B has been isolated for platinum (*12*). A π-adsorbed cyclopropane (C), first proposed by Addy (*13*) [see also Addy and Bond (14) and Newham (15)], has also been retained by most workers, although recent *ab initio* calculations have shown that cyclopropane cannot form a π complex as does ethylene (*16*).

The choice between species A and B is difficult. The replacement of hydrogen by deuterium in the hydrogenation of cyclo-

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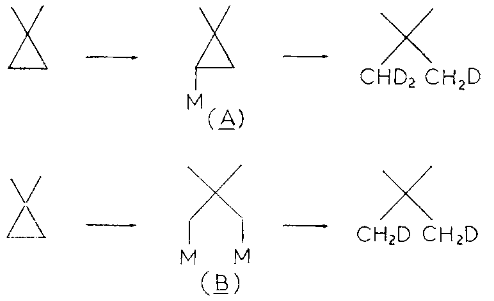
propane is not very useful since the species formed by ring cleavage are extensively exchanged before desorption (*7, 9, 14, 17, 18*). The use of gemdimethylcyclopropane (I) instead of cyclopropane, in the deuteration study proposed by Prudhomme and Gault (*8*), improved the tracer technique. Since the exchange cannot propagate beyond a quaternary carbon atom (*19, 20*), the deuterogenation of (I) distinguishes between type B adsorption, yielding 1,3,d_2-neopentane, and type A, which gives 1,1,3,d_3-molecules.



Of the six metals investigated (Pt, Pd, Rh, Fe, Co, and Ni) only Pt catalyzes the deuterogenation of cyclopropanes dissociatively (type A adsorption) (*8, 21*). 1,1,3,3-Tetradeuteroneopentane has also been found on Pt film, suggesting the formation of $\alpha\beta$-diabsorbed gemdimethylcyclopropane.

Rate-Determining Step

Early proposals that the rate-determining step was the adsorption of cyclopropane to form an $\alpha\gamma$-diadsorbed species (B) (*15*) or the hydrogenation of an adsorbed cyclopropyl (A) (*17*) are no longer considered. Some careful workers, using adsorption and kinetic measurements combined (*24*) or a wide range of temperatures and partial pressures (*25*), suggested that the rate-determining step was a surface reaction between adsorbed cyclopropane and an adsorbed hydrogen atom:

$$(C_3H_6)_{ads} + H_{ads} \rightarrow (C_3H_7)_{ads}.$$

However, the kinetic results were not accurate enough to eliminate the possibility of a reaction involving an adsorbed hydrogen molecule:

$$(C_3H_6)_{ads} + (H_2)_{ads} \rightarrow C_3H_8.$$

On the other hand, the nature of the adsorbed cyclopropane, i.e., whether it is physically adsorbed, π-bonded, or $\alpha\gamma$-diadsorbed, and the existence of the latter species are still debatable.

Relation between Hydrogenation and Hydrocracking

One may ask whether hydrogenation and hydrocracking of cyclopropane take place on different sites, via different adsorbed species, or whether these are parallel steps stemming from a common intermediate. Kinetic arguments have been given in favor of parallel reactions, with either an adsorbed propyl radical (*26, 27*) or an $\alpha\gamma$-diadsorbed species (*28, 9*) as common intermediate. The latter species has the advantage that, by dehydrogenation, it forms the $\alpha\alpha\gamma$-triadsorbed species thought to cause hydrocracking of acyclic hydrocarbons (*29*). However, changes in selectivity (hydrocracking/hydrogenation ratio) with time (*2*), carrier, and pretreatment procedure (*5*) strongly suggest that two different types of sites might be involved in the two reactions. This view is strengthened by the effect of alloying, which is very different for the two reactions (*30*). Moreover, the order of activities of the various transition metals is very different for ring opening and cracking (*6*), probably because different types of species intervene. During the self-hydrogenation of cyclopropane, hydrocracking also takes place, and cyclopropyl-adsorbed species (A) may be a common intermediate (*10, 11*).

In order to clarify all these problems, we systematically studied the deuteration of gemdialkylcyclopropanes on metal catalysts. Use of these molecules permits distinction between "associative" adsorption, involving simple ring cleavage, and "dissociative" adsorption, forming an adsorbed cyclopropyl intermediate (*8, 31*). Moreover, substituted cyclopropanes, because of their structure, may provide more information on the mechanism of hydrocracking than would cyclopropane. Gemdiethylcyclopropane, rather than gemdimethylcyclopropane, was chosen as a model because its major acyclic product, 3,3-dimethylpentane, has two fragments in the mass spectrum, $C_6H_{13}^+$ and $C_5H_{11}^+$, instead of neopentane's one, $C_4H_9^+$; this characteristic facilitates location of the deuterium.

The study is presented in three papers: The first (this paper) deals with the mode of adsorption of gemdialkylcyclopropane and the mechanism of hydrocracking on various metal catalysts, while the next two (*23a, b*) are on the nature of the rate-determining step.

EXPERIMENTAL

Apparatus and Procedure

Catalytic experiments were carried out in a conventional static system (*32*), with the reaction vessel (200 ml) connected to and A.E.I. MS-2 mass spectrometer so that the reaction could be followed with time. A mixture of deuterium and hydrocarbon is introduced on the freshly prepared film or on the pretreated supported catalyst at the reaction temperature. The experimental conditions were such that the rate of exchange of the acyclic products was 80–200 times smaller than the rate of cyclopropane deuterolysis. When the reaction was completed, which was within a few minutes except in the experiments on gold, the final mass spectrum was recorded, and the hydrocarbons were removed for glc analysis. When several compounds were present, the molecules were separated by gas chromatography, and their mass spectra were recorded to determine the deuterium distribution. In one experiment on gold, several samples (5% of the total mixture) were removed for glc analysis in order to follow the change with time of the various product concentrations.

Catalysts

Au and Co films were prepared by heating, under 10^{-6} Torr, very fine wires wound around 0.3-mm tungsten wire. The preparation of the other metal films has already been described (*33*). Specpure samples were obtained from Johnson Matthey. The supported catalysts (10% Pt–Al_2O_3 and 10% Ir–Al_2O_3) were prepared by impregnating a very pure γ-alumina obtained from Woelm A. G. with chloroplatinic acid or iridium tetrachloride. The size of the metal particles, determined by X-ray line broadening, was around 160 Å, and the accessibility of the Pt, determined by hydrogen-oxygen titration, was about 5%.

The alumina powder was calibrated at 100–200 mesh to minimize the influence of interparticle diffusion (*43*). We verified that gemdialkylcyclopropane did not react on alumina at less than 100°C.

Before each catalytic experiment, the supported catalyst was outgassed several times under 10^{-5} Torr and was allowed to adsorb pure deuterium at room temperature until we detected no hydrogen–deuterium exchange. This prodecure exchanges five times as much hydrogen as could reasonably be adsorbed on the Pt surface according to the accessibility measurement, showing that both the hydrogen adsorbed on the platinum and the hydrogen of the hydroxyl groups of the alumina reacted. We believe that the metal catalyzes the exchange with deuterium of the alumina OH groups by some spillover effect (*34*), since this reaction does not take place on pure alumina at less than 100°C.

Materials

Gemdiethylcyclopropane was prepared as described by Bartleson *et al.* (*35*). Gemdimethylcyclopropane was synthesized in two steps by converting the 2,2-dimethyl-1,3-propanediol into its 1,3-dibromide form and cyclizing it in the presence of Zn (*36*). Both cyclopropane hydrocarbons were purified by distillation over sodium and by gas–liquid chromatography. 3,3-dimethylpentane, 2-methylbutenes, and neopentane were obtained from Fluka or Aldrich (Puriss. grade). The deuterium, purified by passage through a palladium thimble, had an isotopic purity of 99%.

Perdeuteroisobutane, C_4D_{10}, was prepared by repeated exchange of C_4H_{10} with deuterium on a tungsten film.

Gas–Liquid Chromatographic Analysis

Cyclopropane and acyclic saturated hydrocarbons were separated on a 5-m, $\frac{1}{4}$-in., 40% dimethylsulfolane/firebrick column (or a 5-m, $\frac{1}{4}$-in., 20% SE 30/firebrick column when light hydrocarbons were present). The olefins obtained in the reaction of gemdimethylcyclopropane on Au and W were analyzed and separated at 0°C on a 5-m, $\frac{1}{8}$-in. column filled with 20% OV1 methyl silicone on Chromosorb.

Mass Spectrometric Analysis

All mass spectra were obtained using 25 eV.

3,3-Dimethylpentane, neopentane, isopentane, and isobutane. Since the parent ion is negligible in the mass spectrum of 3,3-dimethylpentane and neopentane and minor in the mass spectra of isobutane and isopentane, the demethylated fragments $C_{n-1}X_{2n-1}^+$ (pseudoparent ions with $X = H$ or D) were used to characterize the deuterium distributions.

The fragment ions $C_{n-1}X_{2n-2}^+$ and $C_{n-1}X_{2n-3}^+$ are reported in Table 1 and are expressed as a percentage of the pseudoparent ions. In the case of neopentane and 3,3-dimethypentane, the two fragments are very small and the corrections for fragmentation were made statistically, neglecting the isotope effect (*37*). The same calculations were made for the butyl ion formed from isopentane, although the fragment $C_4H_8^+$ is rather large. In the case of isobutane, the difference in fragmentation between the light and the heavy molecules, although very small, was taken into account.

3,3-Dimethylpentane (de-ethylated fragment). Together with the pentyl ion $C_5H_{11}^+$, a major fragment, $C_5H_{10}^+$, and a minor one, $C_5H_9^+$, are present in the mass spectrum of light 3,3-dimethylpentane. In order to account for the isotopic effect in the C–H, C–D fragmentation, the mass spectrum of $(C_2H_5)_2C(CH_2D)_2$, formed by deuterolysis of gemdiethylcyclopropane on nickel, was also recorded and the fragments $C_5H_9D^+$ and $C_5H_9^+$ were computed (Table 1). The distributions of the pentyl ions obtained from a mixture of deuterodimethylpentanes

TABLE 1

Mass Spectra of Various Labeled and Unlabeled Hydrocarbons

Hydrocarbon	Formula	$C_{n-1}X_{2n-1}^+$	$C_{n-1}X_{2n-2}^+$	$C_{n-1}X_{2n-3}^+$
d_0-3,3-Dimethylpentane	$(CH_3)_2C(C_2H_5)_2$	100	3.6	0.8
d_0-Neopentane	$(CH_3)_4C$	100	4.4	2.8
d_0-Isopentane	$(CH_3)_2CH\ C_2H_5$	100	31.5	9.2
d_0-Isobutane	$(CH_3)_3CH$	100	32	40
d_{10}-Isobutane	$(CD_3)_3CD$	100	33	34

Hydrocarbon	Formula	$C_5H_9X_2$	$C_5H_9X^+$	$C_5H_9^+$
d_0-3,3-Dimethylpentane $X = H$	$(CH_3)_2C(C_2H_5)_2$	100	30	0.2
d_2-3,3-Dimethylpentane $X = D$	$(CH_2D)_2C(C_2H_5)_2$	100	16	0.1

were then calculated after statistical correction for the $C_5X_{10}^+$, and $C_5X_9^+$ ions (*37*), assuming a random rupture of all 11 C–X bonds in $C_5X_{11}^+$.

2-methyl But-1-ene and 2-methyl but-2-ene. The deuterium distribution patterns for these molecules were obtained from the parent ions. Since the two first fragments at mass $m/e = 69$ and 68 are small, the corrections for fragmentation were made neglecting any isotope effect.

Gemdimethylcyclopropane and gemdiethylcyclopropane. The mass spectrum of gemdiethylcyclopropane includes, besides a substantial molecular ion ($m/e = 98$), a large fragment at mass $m/e = 83$ and two at masses $m/e = 70$ and 69. During the reaction $D_2 + C_7H_{14}$, on all the metals for which it was investigated (Pt, Pd, Ir, Au), no ions with masses 99 or greater appeared in the mass spectrum of the reaction mixture. This shows that no exchanged cyclopropane is obtained in the gaseous phase, and, since the mass spectrum of the gemdiethylcyclopropanes does not interfere with the spectra of the acyclic products in the C_6^+ and C_5^+ regions, the reaction can be followed with time. Similar considerations hold for the reaction of gemdimethylcyclopropane with deuterium.

RESULTS

I. Deuterolysis of Gemdiethylcyclopropane

(*a*) *Nickel and palladium.* The deuterolysis of gemdiethylcyclopropane was studied on palladium at 0°C and on nickel at −37°C, 3,3-Dimethylpentane is the

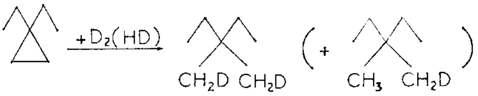
TABLE 2

Deuterolysis of Gemdiethylcyclopropane on Various Metal Catalysts

	Catalyst				
	Ni film	Pd film	Pt film	10% $Pt-Al_2O_3$	10% $Ir-Al_2O_3$
T (°C)	−37	0	−16	−16	−18
P_{HC} (Torr)	1.3	1.7	3.3	3.3	3.3
P_{D_2} (Torr)	16.7	16.7	10.	10.	10.
Pentyl ions (%)					
p_0	0	0	0.6	0.6	0
p_1	6.9	6.4	10.5	12.7	6.1
p_2	93.1	93.6	79.0	52.9	87.4
p_3	0	0	7.4	19.6	3.9
p_4	0	0	2.5	14.2	2.6
Hexyl ions (%)					
h_0	3.9	3.4	5.5	9.0	4.3
h_1	96.1	96.6	88.8	72.7	90.4
h_2	0	0	4.3	10.3	3.2
h_3	0	0	1.4	8.0	2.1
Deutero species (%)					
P_2	100	100	87.6	58.1	92.7
P_3	0	0	9.0	18.7	4.1
P_4	0	0	3.4	23.2	3.2
P_4'	0	0	0	0	0
y	0.037	0.033	0.06	0.11	0.04

major reaction product. Only 2.5 and 0.5% of 3-ethylpentane are formed on nickel and palladium, respectively. For 3,3-dimethylpentane, the deuterium distributions of the various demethylated (hexyl: h_i) and deethylated (pentyl: p_i) fragments are given in Table 2.

These distributions, which do not extend beyond the d_1-hexyl ion and the d_2-pentyl ion, with a percentage of the hexyl ion h_0 approximately half that of the pentyl ion p_1, are consistent with the presence of only two deuteromolecules, namely, the monodeuterodimethylpentane $[(C_2H_5)_2C(CH_3)(CH_2D)]$ (6–7%) and the dideuterodimethylpentane $[(C_2H_5)_2C(CH_2D)_2]$ (94–93%). These obviously result from the simple addition of D_2 (or HD) to the cyclopropane ring.

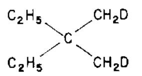


The amount of the monodeutero molecule, about three times that expected from the observed isotopic dilution of the gaseous hydrogen (about 1%), clearly indicates an isotopic effect.

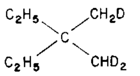
(*b*) *Platinum and iridium.* The deuterolysis of gemdiethylcyclopropane on platinum films and on 10% Pt–Al_2O_3 and 10% Ir–Al_2O_3 was studied under various experimental conditions. 3,3-Dimethylpentane was the only reaction product. The deuterium distributions of the pentyl and hexyl ions for three typical experiments are given in Table 2. They include d_0- to d_3-hexyl ions and d_6- to d_4-pentyl ions, with pronounced maxima at p_2 and h_1. The complete lack of d_5- and d_6-pentyl ions shows that a maximum of four deuterium atoms are present on the methyl groups. Moreover, if one assumes that, as a result of the deuterolysis of the cyclopropane ring, at least one deuterium atom is present on each methyl group in the most deuterated species, the absence of hexyl ions beyond d_3 shows that the ethyl group contains no more than two deuterium atoms. In spite of these limitations, there are many possibilities for the distribution of the deuterium atoms among the ethyl and the methyl groups in 3,3-dimethylpentane.

The absence of exchange between deuterium and 3,3-dimethylpentane, especially on the ethyl groups, under the same experimental conditions, and the fact that the exchange of an adsorbed molecule cannot propagate beyond a quaternary carbon atom suggest the presence of only four deutero species:

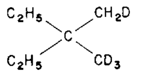
P_2



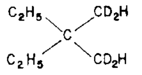
P_3



P_4



P'_4



On the other hand, the presence of small but definite amounts of d_1-pentyl (p_1) and d_0-hexyl (h_0) ions shows that, besides P_2, P_3, and P_4, less deuterated species should be envisaged, the result of an isotopic dilution of the deuterium by the light hydrogen present in the reaction mixture or arising during the formation of P_3 and P_4. The mole fraction y of hydrogen and the values of P_2, P_3, and P_4 may be determined by solving a set of equations that express the percentage of the various deuteropentyl and -hexyl ions as a function of P_i and y.

Although this set, developed in the Appendix, includes seven independent equations with four unknowns, it can be solved exactly, justifying the choice of P_2, P_3, P_4, and P_4' as the only reaction products.

The values found for P_i and y are re-

TABLE 3

Deuterolysis of Gemdiethylcyclopropane on Platinum Catalysts: Percentages of the Various Deutero Species

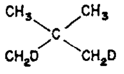
Run	Catalyst	*T* (°C)	P_{HC} (Torr)	P_{D_2} (Torr)	P_2	P_3	P_4	P_4'
1	10% Pt-Al_2O_3	−16	3.3	10	56.7	18.1	25.2	0
2		0	3.3	10	52.8	17.9	29.0	0.3
3		−16	3.3	100	72.1	17.4	10.5	0
4		−16	3.3	10	58.1	18.7	23.2	0
5	Pt film	−16	3.3	100	91.4	6.6	2.0	0
6		−16	3.3	10	87.6	9.0	3.4	0

ported in the last rows of Table 2. The trideutero species P_3 and the asymmetrical tetradeutero species P_4 (but not the symmetrical one P'_4) are formed in appreciable amounts (more than 40%) on Pt–Al_2O_3 at −16°C. On Pt films and Ir–Al_2O_3, these species represent only 12 and 7% of the products, respectively. The values found for *y* in all three experiments are about twice those expected, taking into account the hydrogen present in the deuterium gas or that produced during formation of P_3 and P_4. Table 3 gives the various values found for P_i when changing the experimental conditions. Deuterium distributions were reproducible (runs 1 and 4). An increase in temperature only slightly increased the P_4/P_2 ratio (runs 1 and 2), and an increase in deuterium pressure significantly decreases the amounts of P_3 and P_4 (runs 3–6).

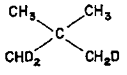
II. Deuterolysis of Gemdimethylcyclopropane

(*a*) *Palladium, rhodium, platinum, and iridium.* The deuterolysis of gemdimethylcyclopropane was studied on Pd, Rh, and Pt films between -20 and 20°C and on 10% Pt–Al_2O_3 and 10% Ir–Al_2O_3 at 0°C. The products were more than 99% 2,2-dimethylpropane (neopentane). The deuterium distributions of the tert-butyl (t-butyl) ions obtained from this molecule by electron bombardment are reported in Table 4. For Rh and Pd films, these consist of d_1 and d_2 in equal amounts. Moreover, no t-butyl ions beyond d_2 are formed, which shows that the only reaction product is $(CH_3)_2C(CH_2D)_2$, P_2, resulting from simple addition of a deuterium molecule to gemdimethylcyclopropane.

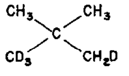
For Pt and Ir, trideutero and tetradeutero t-butyl ions are present in appreciable amounts. Previous results obtained in deuterolysis of gemdiethylcyclopropane suggest that four deutero molecules are formed.



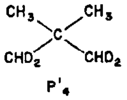
P_2



P_3



P_4



P'_4

These molecules give rise to mass spectra showing t-butyl ions containing from one to four deuterium atoms. To account for the d_0 t-butyl ion one has to assume that an isotopic dilution of the deuterium takes place. Equation set (2) (Appendix) relates the percentages, d_i, of the t-butyl ions $C_4H_{9-i}D_i^+$ to the percentage, P_i of the deutero neopentanes and to *y*, the mole fraction of reacted light hydrogen. Set (2)

TABLE 4

Deuterolysis of Gemdimethylcyclopropane on Rhodium, Palladium, Platinum, and Iridium Catalysts

	Catalyst										
	Rh film	Pd film		Pt film						10% $Pt{-}Al_2O_3$		10% $Ir{-}Al_2O_3$
T (°C)	0	0	20	−20	0	20	30	30	30	0	0	0
P_{HC} (Torr)	3	3	3	3	3	3	1.7	1.7	1.7	1.7	1.7	3.3
P_{D_2} (Torr)	30	30	30	30	30	30	6.7	16.7	67	6.7	71	10
Neopentane (t-butyl ions) (%)												
d_0	0.15	0.0	0.35	1.05	0.95	0.65	3.5	1.3	0.5	4.9	0.8	1.8
d_1	49.5	49.6	50.0	46.6	45.95	44.0	43.7	43.0	43.9	37.7	38.0	47.7
d_2	49.0	50.2	49.7	44.6	43.95	41.6	37.7	40.9	44.7	28.7	34.8	45.0
d_3	1.0	0.2	—	5.5	7.0	9.8	11.0	10.8	8.1	18.1	16.2	3.7
d_4	0.4	<0.1	—	2.2	2.1	3.9	4.1	4.5	2.8	10.6	10.2	1.8
d_5	—	—	—	0.04	0.07	0.08	—	<0.1	—	—	—	—
Deutero species (%)												
P_2	100	100	100	85	82	75	69	70	78	45	54	88.2
P_3	0	0	0	10	13	17	21	20	16	23	24	7.6
P_4	0	0	0	2	3	6	6	4	0	28	17	0
P_4'	0	0	0	3	2	2	4	6	6	4	5	4.2

TABLE 5

Deuterolysis of Gemdimethylcyclopropane on Cobalt, Iron, and Nickel Films

	Catalyst						
	Co	Co	Co	Fe	Fe	Ni	Ni
T (°C)	0	0	41	0	41	0	50
P_{HC} (Torr)	1.7	1.7	1.7	1.7	1.7	3	1.7
P_{D_2} (Torr)	20	20	20	20	20	30	20
Neopentane (t-butyl ions) (%)							
d_0	2.4	4.5	8.5	1.8	6.5	0.8	11.8
d_1	50.4	51.4	49.5	49.3	52.5	50.2	51.9
d_2	46	42.8	36.9	47.1	39.2	48.9	35.7
d_3	0.9	0.9	4.0	1.0	1.2	0.1	0.5
d_4	0.3	0.3	1.0	0.8	0.6	0	0.1
d_5	0.03	0.03	0.1	0	0	0	—
Neopentane (%)	84.4	85.2	76.4	72.2	76.3	100	68
Isobutane (%)	14.5	11.3	22.1	27	22	—	26.1
Isopentane (%)	1.1	3.5	1.5	0.8	1.7	—	5.9

consists of four independent equations with four unknowns and may be solved exactly.

The values of P_i are reported in the last rows of Table 4. As in the deuterolysis of gemdiethylcyclopentane, supported Pt–Al_2O_3 catalysts favor the formation of the trideutero and tetradeutero molecules (ca. 50%). The amounts of P_3, P_4, and P_4' on Pt films are much smaller (15–30%) and increase when the temperature is increased or when the deuterium pressure is decreased. Both the asymmetrical and symmetrical tetradeutero species, P_4 and P_4', are formed, the latter being relatively more important when the total amount, $P_4 + P_4'$, is small. As for gemdimethylcyclopropane deuterolysis, very few tri- and tetradeutero molecules are formed on Ir; these are the trideutero species P_3 and the symmetrical tetradeutero species P_4'.

(*b*) *Cobalt, iron, and nickel.* The deuterolysis of gemdimethylcyclopropane was studied on Co, Fe, and Ni films between 0 and 50°C. Besides neopentane, appreciable amounts of isobutane are formed on each metal and also, especially on Ni, isopentane, resulting from the rupture of the quaternary–secondary C–C bonds. Propane and ethane were not detected.

The deuterium distributions of the t-butyl and propyl ions obtained from the isopentanes and isobutanes, respectively, are reported in Table 6. The predominance of perdeutero ions $C_4D_9^+$ and $C_3D_7^+$ in every experiment shows that isopentanes and isobutanes are widely exchanged. This extensive exchange partly explains the abnormally high amount of d_0 t-butyl ion $C_4H_9^+$ obtained in the mass spectra of the neopentanes (Table 5).

The definite traces of d_3 and d_4 t-butyl ions in the mass spectra of the neopentanes obtained on Co and Fe films show that trideutero and tetradeutero molecules are formed, especially at high temperatures.

III. Deuterolysis and Isomerization of Gemdialkylcyclopropane on Tungsten and Gold

(*a*) *Tungsten.* Gemdimethylcyclopropane reaction with hydrogen or deuterium on W films yields a mixture of neopentane and isopentane (*38*). For example, at 0°C, 70–88% and, at 300°C, 97–98% of the reaction products consist of deutero isopentanes. The "abnormal" rupture of the quaternary–secondary C–C bond cannot be accounted for by a contamination of the W film: when 10^{-2} Torr of air or oxygen was admitted on freshly evaporated W film, no reaction was observed.

In order to determine the role of hydrogen in the formation of isopentane, two experiments were done at 203°C, in the absence and in the presence (60 Torr) of hydrogen. The hydrogenolysis of gemdimethylcyclopropane yields 93% isopentane and 4% isobutane, in agreement with Muller's results (*38*). In the absence of hydrogen, we obtained 96.5% 2-methylbutenes, mainly 2-methyl-but-2-ene and 2-methyl-but-1-ene in the ratio 6.4 to 1, and 2% isobutene. In the hydrogenolysis experiments, then, isopentane is probably formed by isomerization of the gemdimethylcyclopropane and hydrogenation of the resulting olefins.

This view is confirmed by the contact reactions of gemdiethylcyclopropane on W at 50°C in the presence and in the absence of hydrogen. In both cases, the same amount (86%) of hydrocarbons with the 3-ethylpentane skeleton is obtained. In the presence of hydrogen, the product distribution includes, besides 3-ethylpentane, 6.6% of 3,3-dimethylpentane, formed by the "normal" hydrogenolysis of the CH_2–CH_2 bond, and 7.3% of 3-methylpentane, a cracking product. In the absence of hydrogen, besides 3-ethyl-pent-2-ene and 3-ethyl-pent-1-ene (in the ratio of 70 to 1), 10% of *cis*- and *trans*-3-methyl-pent-2-ene are obtained.

(*b*) *Gold.* On Au films, gemdimethylcyclopropane, in the presence or absence of hydrogen, reacts only at 375°C, isomerizing to the three isomers of methylbutene in various concentrations (Fig. 1). 2-Methyl-but-2-ene and 3-methyl-but-1-ene, formed initially in approximately equal amounts, yield 2-methyl-but-1-ene as a secondary product. The presence of hydrogen in the reaction mixture increases the isomerization rate by a factor of 10. Equilibrium among the three methylbutenes is achieved at a conversion as low as 10%.

TABLE 6

Deuterium Distributions of the Isopentanes and Isobutanes Formed on Nickel, Cobalt, and Iron Films (Pseudoparent Ions)

	Catalyst			
	Co	Co	Fe	Ni
	0°C	41°C	41°C	50°C
Isobutane (%)	11.3	22.1	22.0	26.1
Propyl ions[a]				
d_0	1.0	1.0	3.1	0.0
d_1	6.7	1.1	2.6	2.5
d_2	5.6	2.8	6.6	6.4
d_3	3.9	2.7	4.2	7.4
d_4	9.8	2.9	6.6	6.3
d_5	6.5	5.7	9.9	9.4
d_6	15.7	21.3	20.8	23.6
d_7	50.8	62.5	46.2	44.4
Isopentane (%)		1.5		5.9
Butyl ions[b]				
d_3		7.4		21.4
d_4		18.3		23.4
d_5		13.9		32.5
d_6		20.3		34.1
d_7		18.3		32.1
d_8		49.1		67.9
d_9		100		100

[a] Expressed as a percentage of the $C_3X_7^+$ ions.

[b] Ion current related to $C_4D_9^+$ taken as 100.

To determine the role of hydrogen in the isomerization of gemdimethylcyclopropane on Au the two major isomers formed in the presence of deuterium gas were analyzed for their deuterium content. The distributions (Table 7) show an extensive incorporation of deuterium, much greater than for the olefin isomerized under the same conditions (third and fourth columns).

A study of the isomerization of gemdiethylcyclopropane on Au film at 400°C confirms these results. The presence of hydrogen in the reaction mixture increases the reaction rate considerably. Initially

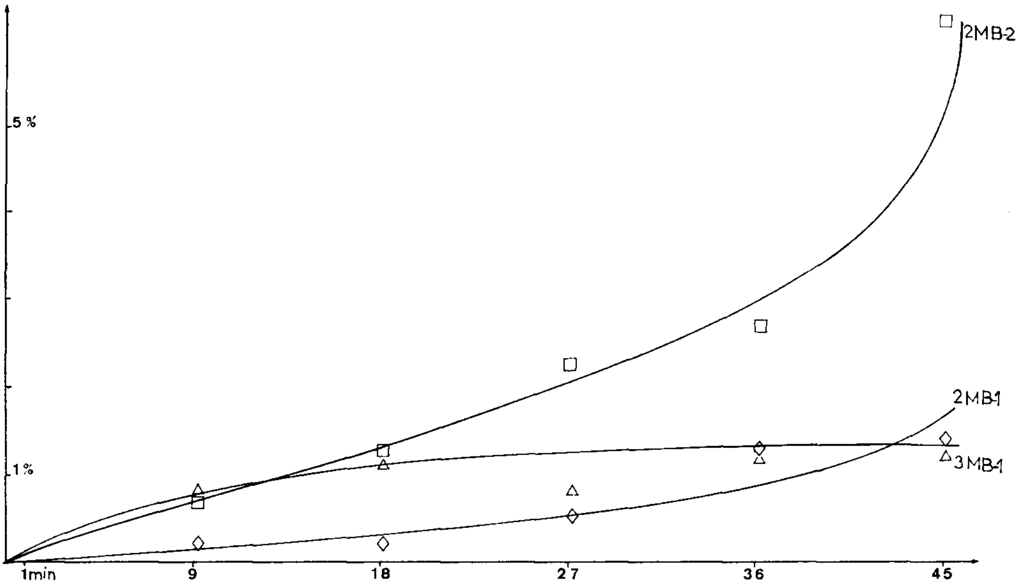


FIG. 1. Variations with conversion of the concentrations of the three methylbutene isomers (gold film): 3 MB-1, 3-methyl-but-1-ene (△); 2 MB-2, 2-methyl-but-2-ene (□); 2 MB-1, 2-methyl-but-1-ene (◇).

3-ethyl-pent-1-ene and 3-ethyl-pent-2-ene are formed approximately in the ratio of 2 to 1, but a very fast equilibration of the two olefins takes place as a successive reaction: The product distribution at 10% conversion is close to that at equilibrium.

TABLE 7

Deuterium Distribution of the Two Methyl Butenes Obtained from Gemdimethylcyclopropane or 2-Methyl-but-1-ene on Gold Films at 375°C

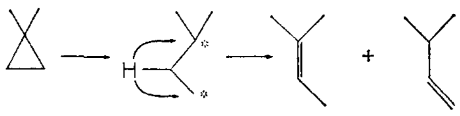
	Reacting hydrocarbon			
	Gemdimethylcyclopropane		2-Methyl-but-1-ene	
Isomerization (%)	18		59	
Product (%)	2-MB-1 (29)	2-MB-2 (65.5)	2-MB-1 (41)	2-MB-2 (56)
Deuterium distribution $\sum_{1}^{10} d_i = 100$				
d_1	5.5	6.2	7.6	12.7
d_2	6.9	7.2	21.4	24.7
d_3	6.0	9.6	29.1	28.1
d_4	10.4	11.5	23.9	19.9
d_5	16.5	14.2	12.1	9.1
d_6	18.5	15.8	4.1	3.3
d_7	14.0	14.7	0.9	1.2
d_8	8.2	9.6	0.6	0.8
d_9	7.7	6.5	0.2	0.1
d_{10}	6.3	4.7	0.2	0.1
$M = \sum_i d_i/100$	5.8	5.5	3.3	3.1

DISCUSSION

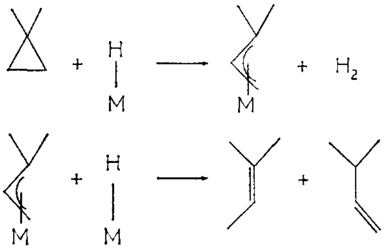
Hydrogenolysis and Isomerization

For gemdimethyl- and gemdiethylcyclopropane on all metals except W and Au, the ring cleavage occurs usually, if not exclusively, at the bond opposite the quaternary carbon atom. Alkyl substituents affect the position of hydrogenolysis (*2*, *25*, *39–44*), and steric or electronic factors may explain it (*2*, *9*, *14*, *24*, *45*).

On W, however, methylcyclopropane (*9*) and gemdimethylcyclopropane (*38*) also break at the bond adjacent to the point of substitution. This "abnormal" ring cleavage in the absence of hydrogen, yielding olefins, clearly shows that gemdialkylcyclopropane isomerizes on W much as it does on acidic catalysts. In the presence of hydrogen, this isomerization, followed by very rapid hydrogenation of the resulting olefins, competes with the "normal" hydrogenolysis. Isomerization of gemdialkylcyclopropane and double-bond migration in the resulting olefins were always very rapid on W films, even at low temperatures, so that we could not determine the structure of the primary products. On Au, where the reaction is slow, the initial distribution is formally consistent with a ring cleavage of the most substituted C–C bond followed, by an α–β hydride shift.



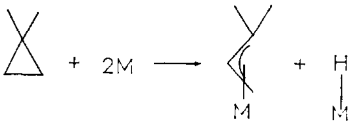
The high reaction temperature, corresponding to that at which molecular hydrogen is dissociatively adsorbed on Au (*46*), the rate increase in the presence of hydrogen, and the extensive incorporation of deuterium into the reaction products when deuterium replaced hydrogen strongly suggest that adsorbed hydrogen (or deuterium) atoms are involved in isomerization. We suggest that, on Au in the presence of hydrogen, gaseous or physically adsorbed gemdimethylcyclopropane reacts with adsorbed hydrogen to yield an adsorbed π-allylic species which is then rehydrogenated to the olefinic products.



(1)

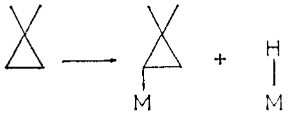
(2)

In the absence of hydrogen, reaction (1) would be replaced by the following more difficult reaction.



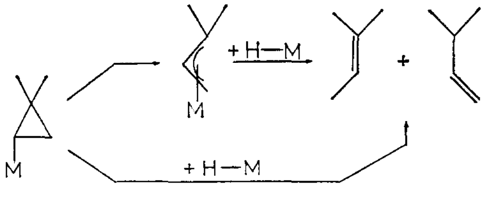
(1')

The mechanism of isomerization on W could be the same as that on Au, except that the extent of isomerization of gemdialkylcyclopropane does not seem to be influenced by the presence of hydrogen. Moreover, cyclopropane hydrocarbons are rapidly exchanged with deuterium on W films, which shows that cyclopropyl-adsorbed species are easily formed (*9*). It is tempting to suggest that these species (A) are precursors for the isomerization reaction.



(3)

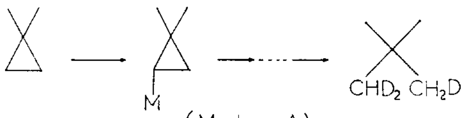
A very rapid cleavage, whether involving allylic species or not, before hydrogenation would then yield the olefinic products.



In the presence of hydrogen, the kinetic law obtained by Anderson and Avery (*9*) for the overall reaction of cyclopropane on W ($r = kp_c^{-1}p_{H_2}^{0.4}$) is very different from that for other metals (positive orders vs hydrocarbon; zero or slightly negative orders vs hydrogen). Moreover, the hydrogenolysis/exchange ratio did not depend upon partial pressures and temperatures. We believe that, on W, in the presence as in the absence of hydrogen, dissociatively adsorbed cyclopropane (*3*) forms before the ring opens.

The Modes of Cyclopropane Adsorption

In the first paper of this series (*8*), the formation of d_3- and d_4-neopentane from gemdimethylcyclopropane was taken as proof of the occurrence of dissociative adsorption.



(Mechan. A)

Of four metals investigated (Pt, Pd, Rh, and Ni) only Pt promoted this mode of adsorption, the most common one being simple ring opening, yielding 1,3-dideuteroneopentane.

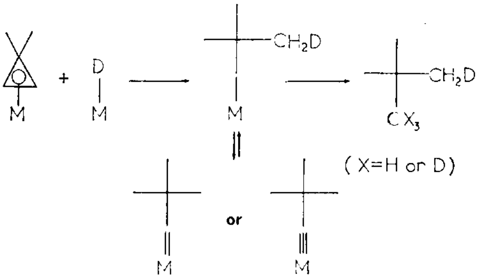
(Mechan. B)

The present study, extended to five more metals (Fe, Co, Ir, W, and Au), confirms the unique behavior of Pt in promoting the dissociative mechanism of hydrogenolysis. Besides Pt, Ir can also do this, but to a much smaller extent, and maybe very slightly can Fe and Co also do this at 40°C. Last, as discussed before, dissociative adsorption takes place extensively on W but leads to isomerization products.

The metals may be classified, then, according to their ability to promote mechanism A.

$$\text{Pt} \gg \text{Ir} \gg \text{Co} > \text{Fe} > \text{Ni} > \text{Rh, Pd}$$

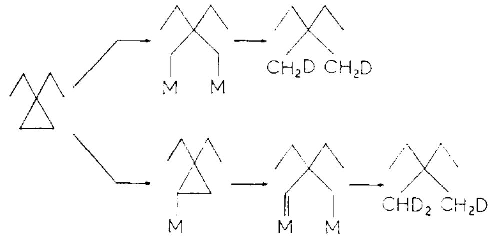
Kemball and Kempling (*22*) found the sequence Co > Fe > Ni in a recent study of the deuterolysis of gemdimethylcyclopropane at high temperatures, but interpreted it differently. Finding the same order of catalytic activities for multiple exchange of neopentane (yielding d_3) and formation of d_4-neopentane from gemdimethylcyclopropane at 200–220°C, they suggested that the highly deuterated species in the latter reaction were formed by extensive exchange of the neopentyl-adsorbed species.



(Mechan. C)

Even if their mechanism is correct at high temperatures, and one could argue against it, it is not applicable to low-temperature deuterolysis. No correlation exists between the initial distributions for the exchange of neopentane [Refs. (*20*) and (*8*) and this work] and the distributions of the deuteroneopentanes obtained by deuterolysis of gemdimethylcyclopropane. Ni and Pd promote the simple exchange of neopentane and the deuterolysis of gemdimethylcyclopropane according to mechanism B. But a quasi-simple exchange of neopentane takes place on Pt, which is the best metal for forming d_3 and d_4 species in gemdimethylcyclopropane deuterolysis. In contrast, only the associative mechanism B occurs on Rh, and this metal is the best catalyst for multiple exchange (*20*). A further reason to reject mechanism C for low-temperature hydrogenolysis is the trace of symmetrical 1,1,3,3,d_4-neopentane obtained on Pt and Ir catalyst in the deuterolysis of gemdimethylcyclopropane. The presence of this species P_4' requires propagation of the exchange from one methyl group to another, which is not possible according to mechanism C.

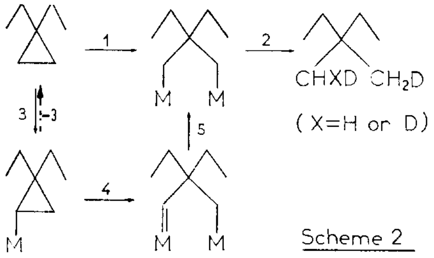
Once mechanism C is eliminated, the question arises as to whether dissociative mechanism (A) and simple ring cleavage (mechanism B) are separate or related. Two models represented in Schemes 1 and 2 may be proposed for the formation of 1,1,3,d_3-dimethypentane in the deuterolysis of gemdiethylcyclopropane.



Scheme 1

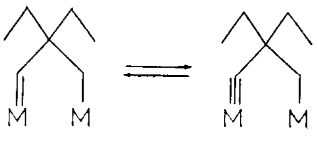
Reversible dissociative adsorption of cyclopropane cannot be accepted in Scheme 2 because it would yield exchanged cyclopropanes and symmetrical d_4 species which are never observed. Therefore, we must eliminate the desorption of the adsorbed cyclopropane (step −3) and suppose a ring cleavage yielding $\alpha\alpha\gamma$-triadsorbed species (steps 4 and 5).

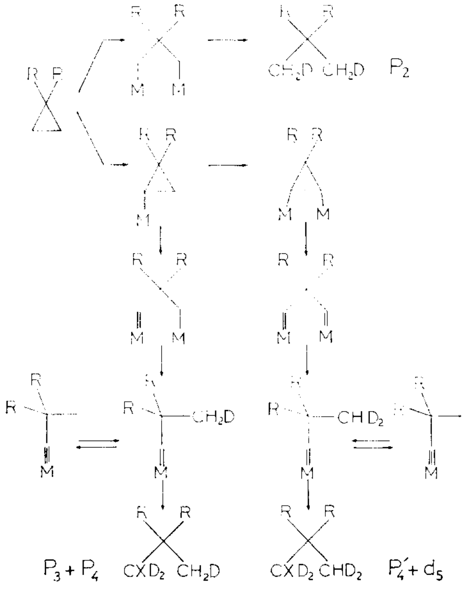
Since d_5, d_6, and symmetrical d_4 species are not obtained under the experimental conditions used, step 5 in Scheme 2 would not be reversible either.



Scheme 2

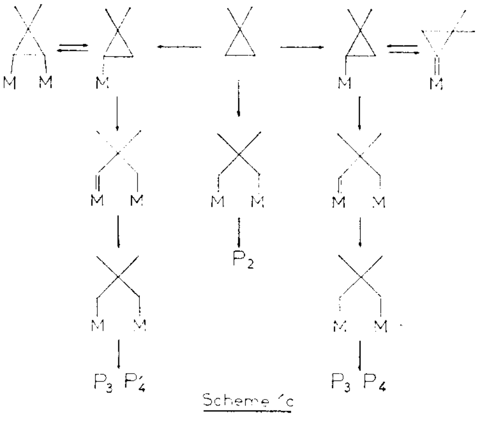
As for the asymmetrical 1,1,1,3,d_4 species P_4, it may be accounted for in three ways: (a) by an interconversion between $\alpha\alpha\gamma$-triadsorbed and $\alpha\alpha\alpha\gamma$-tetra-adsorbed species in scheme 1 or 2; however, $\alpha\alpha\alpha\gamma$ tetra-adsorbed species are very unlikely on account of their geometry; (b) by hydrogenation of the single C–*M* bond in $\alpha\alpha\gamma$-triadsorbed species, followed by interconversion between $\alpha\alpha$-diadsorbed and $\alpha\alpha\alpha$-triadsorbed species. Such a process is only compatible with the assumption that type A and type B deuterolysis are two parallel reactions (Scheme 1b).



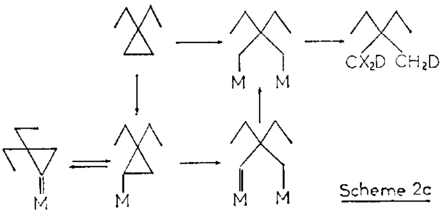


Scheme 1b

(c) Last, by formation of an $\alpha\alpha$-diadsorbed cyclopropane intermediate interconverting with the monoadsorbed species. Such an additional species could be inserted in Schemes 1 (Scheme 1c) or 2 (scheme 2c) as well.



Scheme 1c



Scheme 2c

The formation of symmetrical 1,1,3,3,d_4-species P_4' in gemdimethylcyclopropane deuterolysis necessitates the intervention an an αβ-diadsorbed cyclopropane intermediate, since the complete absence of d_5 and d_6 neopentanes also rules out the formation of P'_4 by interconversion between monoadsorbed neopentyl radicals and αγ-diadsorbed species.

This intermediate is probably formed by elimination of two hydrogen atoms in the *cis* position and could account for the high yield of *n*-pentane on platinum from *cis*- and not *trans*-1,2-dimethylcyclopropane (*47*).

This species cannot be inserted in Scheme 1b since interconversion between αα-diadsorbed and ααα-triadsorbed species would yield d_5 neopentane. If αβ-diadsorbed cyclopropane is inserted into Schemes 1c or 2c, simultaneous interconversion between this species and αα-diadsorbed cyclopropane, on one hand, and monoadsorbed cyclopropane, on the other hand, would also yield d_5 and even d_6 neopentanes. Therefore, we must assume that two types of surface sites exist, on which *either* αβ-diadsorbed cyclopropanes *or* αα-diadsorbed cyclopropanes are formed. This would eliminate the assumption of interrelated route 2c because of the surface heterogeneity, and Scheme 1c thus represents the most probable mechanism for deuterolysis of gemdialkylcyclopropane.

The idea of surface heterogeneity is confirmed and reinforced by the variation of the product distribution (P_2, P_3, P_4, P_4') with metal particle size (*23*).

Hydrocracking of Gemdimethylcyclopropane

Hydrocracking of cyclopropane seems frequent: only Pt, Ir, Rh, and Pd are not active, although McKee obtained methane aud ethane on Pt black at 150°C (*3*). The reaction has been found on Ni (*5*, *6*, *9*, *26*) between −46 and 110°C, on Co (*5*) at 120°C, on Fe (*9*) at 150–170°C, on Os (*28*, *48*) up to 80°C, on Ru (*28*, *48*) between 20 and 250°C, on Re (*27*) at 70–130°C, and on W between −23 and 40°C (*9*). In all cases except on Fe, equimolecular amounts of methane and ethane are formed, showing that only selective hydrocracking takes place:

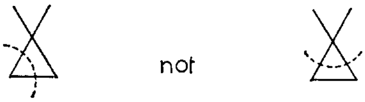
$$C_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6. \quad (1)$$

On the other hand, Fe seems to promote extensive cracking,

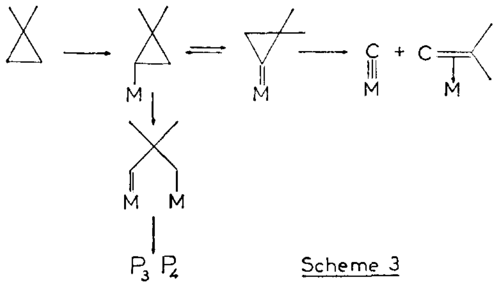
$$C_3H_6 + 3H_2 \rightarrow 3CH_4, \quad (2)$$

perhaps due to the high reaction temperature. At 200°C on Ni hydrocracking of gemdimethylcyclopropane is entirely selective, while on Co and especially on Fe extensive cracking takes place (*22*).

The results presented here agree with other reported data. Fe, Co, Ni, and W were active for hydrocracking of gemdimethylcyclopropane, while Pt, Pd, Rh, and Ir were not. Besides methane, only isobutane was observed in the cracking product. The absence of ethane and propane clearly shows that, on all metals, the ring cleaves at the 1–2 and 2–3 positions and not at the 1–2 and 1–3 positions. Newham and Burwell found a similar selectivity in the cracking of butylcyclopropane (*2*).



Also noticeable is the increase with temperature of the hydrocracking/hydrogenation ratio r: On Ni film, for example, r rises from a negligible value at $-37°C$ to 3 at 210°C. Its increase is accompanied, when going from low (this work) to high temperatures (*22*), by an increase in the percentage of 1,1,1,3,d_4-neopentane P_4, formed by deuterolysis. We believe that this parallel increase for r and P_4 with temperature is not fortuitous and that the same species (i.e., monoadsorbed and αα-diadsorbed cyclopropane) are involved in the production of d_4-neopentane and isobutane.

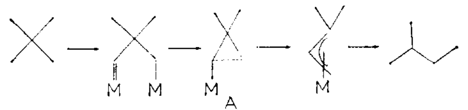


Scheme 3

These species which on Pt yield highly exchanged neopentane may be split into strongly adsorbed residues on easily carbided metals such as Fe, Co, Ni, and W.

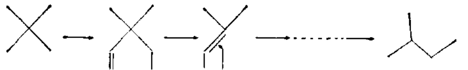
Dissociative adsorption prior to rupture of the carbon–carbon bond in the hydrocracking of cyclopropane was first proposed by Taylor *et al.* (*5*) and was invoked by Merta and Ponec (*11*) to account for the selfcracking on most metals in the absence of hydrogen. Although no definite proofs may be provided in its favor we believe that this mechanism is more likely than the two other ones proposed so far. It is hard to reconcile an adsorbed propyl radical as a precursor in hydrocracking of cyclopropane (*26*, *27*) with the large difference between the rates and activation energies found for that reaction and for hydrocracking of propane. If ααγ-triadsorbed species were the reactive species in cyclopropane hydrocracking (*9*, *28*) it would be hard to explain why Pt, which favors its formation, is such a poor catalyst for this reaction.

Because only Pt can promote both dissociative adsorption of cyclopropane and isomerization of neopentane to isopentane, Muller and Gault proposed that species A could be an intermediate in the latter reaction instead of the proposed Dewar π-complex intermediate (*49*):



Scheme 4

instead of



Scheme 5

The present work shows that, after Pt, Ir is the best metal catalyst for the dissociative hydrogenolysis of gemdimethylcyclopropane. Since Ir is also the only metal besides Pt to catalyze the isomerization of neopentane to isopentane (*50*), the cyclopropane model for bond shift seems attractive. If it is correct, however, then at high temperatures isopentane must be formed together with neopentane in the hydrogenolysis of gemdimethylcyclopropane. Indeed, ring cleavage at the 1, 2 position was observed at 300°C by Muller (*38*), but was so little (5% of isopentane in the reaction products) that consecutive surface reactions of adsorbed species could have occurred, as in the isomerization of dimethylbutanes (*51*). While no evidence yet disproves a bond shift mechanism involving a cyclopropane intermediate, there is also no evidence proving it.

APPENDIX

DEUTERO-3,3-DIMETHYLPENTANES

Equations (A1) Set (1) may be written by assuming a statistical distribution of protium and deuterium in P_2, P_3, P_4, and

TABLE 8

Calculations of the Percentages of Pentyl and Hexyl Ions Using Two Different Fragmentation Corrections

		p_0	p_1	p_2	p_3	p_4	h_0	h_1	h_2	h_3	y	Δ
$n = 11$	Observed	0.7	12.2	51.2	20.7	15.2	8.9	71.7	10.9	8.5	—	
	Calculated	0.8	12.6	50.1	21.1	15.4	9.5	70.9	11.0	8.6	0.12	2.4
$n = 6$	Observed	0.8	14.6	49.5	20.9	14.2	8.9	71.7	10.9	8.5		
	Calculated	1.2	14.6	48.5	21.1	14.6	11.1	69.6	10.9	8.4	0.14	10.6

P'_4:

$$
\begin{aligned}
p_0 &= y^2P_2 + y^3P_3 + y^4(P_4 + P_4'),\\
p_1 &= 2y(1-y)P_2 + 3y^2(1-y)P_3\\
&\qquad + 4y^3(1-y)(P_4+P_4'),\\
p_2 &= (1-y)^2P_2 + 3y(1-y)^2P_3\\
&\qquad + 6y^2(1-y)^2(P_4+P_4'),\\
p_3 &= (1-y)^3P_3\\
&\qquad + 4y(1-y)^3(P_4+P_4'),\\
p_4 &= (1-y)^4(P_4+P_4'), \qquad \text{(A1)}\\
h_0 &= yP_2 + \tfrac{1}{2}y(y+1)P_3 + y^2P_4'\\
&\qquad + \tfrac{1}{2}y(y^2+1)P_4,\\
h_1 &= (1-y)P_2\\
&\quad + (1-y)(y+\tfrac{1}{2})P_3\\
&\quad + 2y(1-y)P_4'\\
&\qquad + \tfrac{1}{2}(1-y)(3y^3+1)P_4,\\
h_2 &= \tfrac{1}{2}(1-y)^2P_3 + (1-y)^2P_4'\\
&\qquad + \tfrac{3}{2}y(1-y)^2P_4,\\
h_3 &= \tfrac{1}{2}(1-y)^3P_4.
\end{aligned}
$$

In the above set of equations, four are selected, which express the percentages of three hexyl ions (h_1, h_2, h_3) and one pentyl ion (p_4), as functions of P_i and y. These equations are linear in P_2, P_3, and P_4' and are solved as such for various values of y, considered as a parameter. Among all the possible solutions, the one that satisfies the normalizing condition is retained:

$$P_2 + P_3 + P_4 + P_4' = 100.$$

h_0, p_0, p_1, p_2, p_3 may then be recalculated: In Table 8, for example, referring to the experiment on 10% Pt–Al_2O_3 at 0°C, calculations were made using two different fragmentation corrections. The first ($n = 11$) assumes that the $C_5X_{10}^+$ ions are obtained by a random rupture of all 11 C–X bonds in $C_5X_{11}^+$; the second ($n = 6$), that only the C–X bonds of the two methyl groups in $C_5X_{11}^+$ are ruptured during the formation of $C_5X_{10}^+$.

From Table 8, a mean square deviation (Δ) may be calculated, and defined as

$$\sum_i [(h_i)_{obs} - (h_i)_{calc}]^2 + \sum_j [(p_j)_{obs} - (p_j)_{calc}]^2.$$

When $n = 11$, $\Delta(2.4)$ is not far from that expected from the experimental errors ($\Delta = 9 \times (0.5)^2 = 2.25$). When $n = 6$, Δ is four times larger. The excellent agreement between calculated and observed values of h_i and p_j with $n = 11$, then, is an *a posteriori* justification of the methods used for the fragmentation corrections.

However, the values of P_2, P_3, and P_4 deduced from the distribution of the deuteropentyl ions are close in both cases. Only the calculated values of y, the concentration of light hydrogen in the reaction mixture, are rather different.

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Equations (A2) may be written by assuming a statistical distribution of protium and deuterium in P_2, P_3, P_4, and P_4' and an equal chance of rupturing any C–C bond when forming t-butyl ions from deuteroneopentanes.

$$
\begin{aligned}
4d_0 &= y\{2P_2(y+1) \\
&\quad + P_3(2y^2+y+1) + 2P'_4y(y^2+1) \\
&\quad\quad + P_4(2y^3+y^2+1)\}, \\
4d_1 &= (1-y)\{2P_2(2y+1) \\
&\quad + P_3(6y^2+2y+1) \\
&\quad + 4P'_4y(2y^2+1) \\
&\quad\quad + P_4(8y^3+3y^2+1)\}, \qquad \text{(A2)} \\
4d_2 &= (1-y)^2\{2P_2 + P_3(6y+1) \\
&\quad + 2P'_4(6y^2+1) \\
&\quad\quad + 3P_4y(4y+1)\}, \\
4d_3 &= (1-y)^3\{2P_3 + P_4(8y+1) \\
&\quad\quad + 8P_4'y\}, \\
4d_4 &= 2(1-y)^4(P_4 + P_4').
\end{aligned}
$$

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