THE CATALYTIC HYDROGENOLYSIS OF SMALL CARBON RINGS

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I. INTRODUCTION

The interaction of a hydrocarbon and hydrogen at the surface of a transition metal or metal oxide may lead to the cleavage of one or more carbon–carbon bonds; such cleavage is termed hydrogenolysis. The hydrogenolysis of an alkane tends to give a complex mixture of products, and studies of these reactions face difficult analytical problems. It is only the recent advent of gas chromatography that has made such studies worthwhile. The lower cycloalkanes, however, hydrogenolyze at relatively low temperatures and yield products which often can be analyzed semiquantitatively by fractional distillation and other methods. By far the larger part of the literature on the catalytic hydrogenolysis of carbon–carbon bonds concerns the cycloalkanes.

This article, then, is mainly concerned with the mechanisms of ring opening during the hydrogenolysis of three-, four- and five-membered carbon rings. The coverage of the literature on the hydrogenolysis of monocyclic rings is intended to be comprehensive, but only a few of the studies on polycyclic rings are included. A number of earlier reviews (15, 25, 41, 101) touch on certain aspects of this subject, but these do not, in general, devote much attention to the reaction mechanisms. The isomerizations of cycloalkanes to olefins on catalysts such as silica or alumina proceed by rather different mechanisms from those involved in hydrogenolysis, and are not considered in this review.

Many of the studies were carried out with catalysts consisting of a metal deposited on a support, the latter usually being chosen for its high surface area and for its inert behavior during the reaction in question. These requirements are not always fulfilled, though, and if the support itself behaves as a catalyst the number of potential mechanisms for a reaction is considerably increased. Thus a reaction might proceed partly on the metal and partly on the support, by way of a migration of adsorbed species across an interface. In addition, the support may influence the electronic state of the metal by forming complexes with individual metal ions, or by allowing an electron transfer to or from metal crystallites. The effects of such phenomena on the mechanisms of catalytic reactions are as yet little understood.

Much of the evidence to be summarized derives from the fractional distillation of mixtures of three or more hydrocarbons of similar boiling points. As a rough guide, the method is usually capable of giving a hydrocarbon concentration accurate to within ±4 mole per cent; it is emphasized that the method is not reliable for the detection of alkanes present in mixtures in concentrations under about 4 mole per cent. Gas chromatography is especially useful in this region, and is probably generally accurate to within ±1 mole per cent.

The main topics are preceded by a short discussion of some relevant properties of the cycloalkanes.

II. SOME PHYSICO-CHEMICAL PROPERTIES OF THE CYCLOALKANES

Raphael (122) and Royals (134) have given general surveys of this topic.

Cyclopropane has carbon–carbon bonds of relatively short length yet of low dissociation energy, and carbon–hydrogen bonds with characteristics similar to those in ethylene (23). A number of other properties, such as the ionization potential (36) and chemical reactivities (95, 125), also resemble those of the simpler olefins. The ring possesses some ability to conjugate with

TABLE I

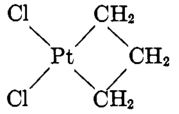
MOLECULAR CONSTANTS OF THE LOWER CYCLOALKANES

References	33, 43, 45				136	123, 132
		Bond lengths and angles			C—C bond dissocn. energies,[a]	Std. free energies of formation $F^\circ_{f298.1}$,
Molecule	C—C, Å.	C—H, Å.	HCH, deg.	CCC, deg.	kcal./mole	kcal./mole
Cyclopropane	1.52	1.07	120	60	57 ± 2	24.98
Cyclobutane	1.56	1.09	114 ± 8	90	70 ± 2	26.31
Cyclopentane	1.54	1.09	109.5	109.5	92 ± 2	9.23
Cyclohexane	1.54	1.10	109.5	109.5	95 ± 2	7.59

[a] The dissociation energies were calculated from the heat of dissociation to the coiled configuration of the biradicals; doubts have been expressed as to the validity of these values (136).

other unsaturated groups (39, 93, 126), but the interactions are much weaker than those of a carbon–carbon double bond, and in addition have certain peculiarities. It appears, for example, that in the ground state, the ring is able to extend a line of conjugation but cannot transmit one (34, 156).

Of special interest is the reaction of cyclopropane with chloroplatinic acid to give a platinum complex which, on treatment with potassium cyanide solution, liberates cyclopropane (155). The expectation that the cyclopropane ring remains intact in the complex (155) now appears to be incorrect, since examination by nuclear magnetic resonance favors a polymeric structure of units linked through chlorine bridges to the platinum (1).



These properties have received several theoretical interpretations (26, 153, 160). According to a treatment by the valence-pairing approximation, the orbitals used by one carbon atom in binding itself to the others diverge at an angle of 104°, so that the line of maximum electron density between two carbon atoms describes a curve. The unusual properties of the carbon–carbon bonds may thus be explained (26). The calculations indicate more p-character in the carbon–carbon bonds, and less in the carbon–hydrogen bonds, than would occur with sp^3 hybridization; the bonding electrons may be considerably delocalized (26).

Cyclobutane has a non-planar ring with a dihedral angle of 20°, and with rather long carbon–carbon bonds (33). It has the highest free energy of formation of all the simple cycloalkanes (Table I). The ring opens much less readily than the three-membered homolog, and has much weaker conjugational interactions with other unsaturated groups (99, 100, 102, 166). Hybridization of the bonding orbitals in cyclobutane is very similar to that in the alkanes (26).

Cyclopentane has a strain-free puckered ring (90) with sp^3 hybridization.

The stabilities of some cycloalkanes relative to the main products of hydrogenolysis are given in Table II. Alkyl substituents stabilize three- and four-membered carbon rings, but have little effect on the five-membered ring. A phenyl substituent quite markedly stabilizes the three-membered ring. Assuming a heat of vaporization of 6.0 kcal. for vinylcyclopropane, the calculated heat of hydrogenation to *n*-pentane is −17.5 kcal.; this excessively low value probably results from errors in the value reported (144) for the heat of combustion of vinylcyclopropane. At temperatures below 600° the thermodynamic equilibria for these reactions favor the formation of alkanes.

TABLE II

HEATS OF HYDROGENOLYSIS OF SOME CYCLOALKANES IN THE GAS STATE AT 25°

Reaction	$-\Delta H^\circ_{h298}$, kcal./mole	Reference
Cyclopropane → Propane	37.6	94
1,1-Dimethyl-2-ethylcyclopropane → 2,2-Dimethylpentane	27.7	56
1,1-Dimethyl-2-propylcyclopropane → 2,2-Dimethylhexane	25.9	56
Spiro-2,2-pentane → 2,2-Dimethylpropane	83.9	37
Phenylcyclopropane → *n*-Propylbenzene	32.9[a]	97
Cyclobutane → *n*-Butane	36.5	55
Methylcyclobutane → *n*-Pentane	31.0	50
Cyclopentane → *n*-Pentane	16.5	89
Methylcyclopentane → 2-Methylpentane	16.2	89
Ethylcyclopentane → 3-Methylhexane	15.6	54
1,1-Dimethylcyclopentane → 2,2-Dimethylpentane	16.2	54

[a] The heat of vaporization of phenylcyclopropane was taken as 10.8 kcal./mole.

III. HYDROGENOLYSIS OF THREE-MEMBERED CARBON RINGS

A. HYDROGENOLYSIS OF CYCLOPROPANE ON METALS

This reaction, first reported by Willstätter and Bruce in 1907 with a nickel catalyst (165), has been the subject of several recent kinetic studies. Bond and co-workers have determined the initial rates manometrically over pumice-supported nickel, rhodium, palladium, iridium and platinum catalysts at 0–200°, with initial reactant pressures in the range 10–500 mm. (2, 10, 11, 12). At a constant initial pressure of cyclopropane, the initial rate varies with increasing hydrogen pressure so as to show a maximum, the position and shape of which depend on the experimental conditions. This behavior is thought to arise from a relatively strong chemisorption of hydrogen on the metal surface, so that as the hydrogen/cyclopropane ratio increases a point is reached beyond which the area of unoccupied surface available for chemisorption of cyclopropane steadily decreases, and the reaction rate falls. The order in cyclopropane is a positive fraction, and tends toward unity at high ratios of hydrogen/cyclopropane. The temperature dependence of the initial rates gives activation energies in the range 9.2 ± 2.5 kcal.; it must be remembered that these values partly depend on the heats of adsorption of the reactants (48).

In an attempt to put these observations on a more quantitative basis, approximate values for the adsorption coefficients of cyclopropane and hydrogen were derived by trial and error comparison of the observed kinetics with those calculated from a Langmuir–Hinshelwood equation (48), the latter based on the assumption that the interaction of adsorbed cyclopropane with an adsorbed hydrogen atom is rate determining. The adsorption coefficient of hydrogen is about ten times that of cyclopropane; both coefficients decrease with increasing temperature. Chemisorption of cyclopropane on rhodium and iridium is stronger than on platinum and palladium (12).

Owing to the use of 4–8 mesh pumice as the catalyst support, these results may have been influenced by a rate-controlling diffusion of the reactants into the catalyst pores; it is unlikely that this introduced serious errors, however, since measurements of hydrogen orders at rates differing by a magnitude of ten were consistent, and most of the experiments were carried out at rates in between the two extremes (12).

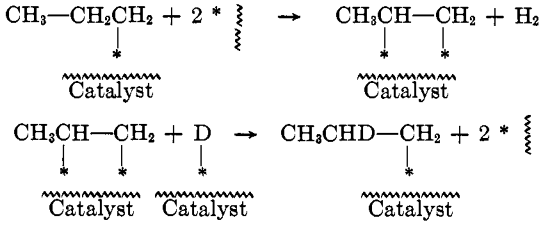
Similar kinetics have been found in studies with other catalysts. On 4% nickel–silica–alumina at 75°, the rates after 25% conversion give orders in cyclopropane and hydrogen of 0.3 and −0.1, respectively, and an activation energy of 15.2 kcal. (9). With commercial iron catalysts containing 0–1.5% potash and maintained at 100–200°, the initial rate is proportional to the cyclopropane pressure and inversely proportional to the hydrogen pressure. As the potash concentration in the catalyst increases, the activation energy rises from 13.5 to 24 kcal., and then falls (46). The causes of the variations in the activation energies found with different catalysts are obscure.

Attempts to analyze mixtures of cyclopropane and propene led to the discovery that the addition of a few drops of mercury to a nickel–kieselguhr catalyst at 150° poisons this material as a catalyst for the hydrogenolysis of cyclopropane, while leaving it active for the hydrogenation of propene (24). This phenomenon has been reinvestigated using a radioactive mercury isotope to follow the extent of poisoning of a nickel film at 25° (20). Chemisorbed layers of cyclopropane or hydrogen are readily displaced from the nickel surface by mercury, whereas an adsorbed propene layer is scarcely affected; the latter, moreover, sterically hinders the adsorption of mercury at the unoccupied surface sites, while allowing the adsorption of hydrogen. Thus the hydrogenation of propene still proceeds in the presence of mercury. The displacement of adsorbed cyclopropane by mercury yields a gas that is not completely condensable at liquid nitrogen temperatures, and might therefore include hydrogen or methane.

The ring cleavage of cyclopropane on pumice-supported metals at 0–200° in the presence of a large excess of deuterium has been followed with a mass spectrometer (2, 3, 4, 11). Over palladium the deuterium content of the gaseous cyclopropane, as found by re-analysis of the products following treatment with concentrated sulfuric acid, never exceeds 1%. In contrast, the reaction on a rhodium film at −78° proceeds with comparable rates of exchange and ring cleavage (6). It is possible that the different results are due to the use of different catalysts. On the other hand, if the catalysts merely differ in their relative activities, the results must imply a higher activation energy for deuterolysis than for exchange (18).

With supported rhodium, palladium and iridium catalysts the initial products of deuterolysis consist mainly of propane-d_8, and the product distributions do not markedly change between 0 and 200°. Platinum behaves differently; at 50° the main initial products are propanes-$d_2 \ldots d_5$, but their concentrations decrease with increasing temperature until at 200° the product distribution resembles those found with the other metals (2, 3, 4). Although cyclopropane-d_0 reacts with deuterium about 200 times faster than does propane-d_0 these two reactions give nearly identical product distributions, except that cyclopropane gives measurably lower concentrations of propanes-$d_1 \ldots d_5$. This difference constitutes about 10% of the total deuterium content of the products, and could result from the formation of di- and triadsorbed cyclopropane species previous to ring cleavage (2–4).

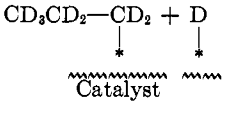
It is clear from these mass-spectrometric studies that the deuterolysis of cyclopropane yields as its primary product adsorbed hydrocarbon radicals, which then undergo multiple exchange with chemisorbed deuterium in the manner



$$CH_3\text{—}CH_2\underset{*}{\underset{\downarrow}{C}}H_2 + 2\,* \rightarrow CH_3\underset{*}{\underset{\downarrow}{C}}H\text{—}\underset{*}{\underset{\downarrow}{C}}H_2 + H_2$$

$$CH_3\underset{*}{\underset{\downarrow}{C}}H\text{—}\underset{*}{\underset{\downarrow}{C}}H_2 + \underset{*}{\underset{\downarrow}{D}} \rightarrow CH_3CHD\text{—}\underset{*}{\underset{\downarrow}{C}}H_2 + 2\,*$$

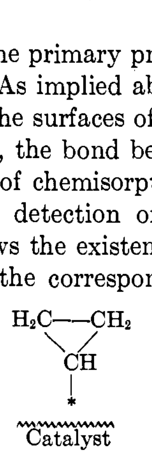
An asterisk represents an active site on the catalyst surface. The final step is the formation of propane by a process such as



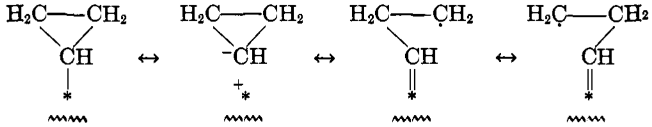
$$CD_3CD_2\text{—}\underset{*}{\underset{\downarrow}{C}}D_2 + \underset{*}{\underset{\downarrow}{D}} \rightarrow C_3H_8 + 2\,*$$

Attempts have been made to interpret the propane–deuterium exchange in terms of simple probability theory, but these have met with rather limited success as yet (84, 85).

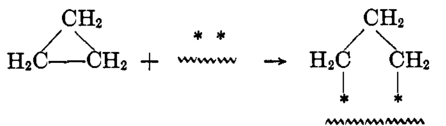
The formation of the primary products may occur in a number of ways. As implied above, the chemisorption of hydrogen at the surfaces of the relevant transition metals is atomic, the bond being mainly covalent (35, 118); the mode of chemisorption of cyclopropane is less certain. The detection of cyclopropane–deuterium exchange shows the existence of adsorbed radicals of type A, and the corresponding 1,2-diadsorbed and 1,2,3-triadsorbed species may also be formed. These radicals could result from the interaction of gas-phase or physically adsorbed cyclopropane with the catalyst surface (2, 11, 19). Once formed, the radicals might be stabilized by resonance involving a carbon–metal double bond of a d-π type (18). Since such conjugative stabilization cannot occur during hydrogenolysis, this proposal would explain a higher activation energy for hydrogenolysis than for isotopic exchange (18). These species might undergo ring cleavage either by interaction with another surface site, or by reaction with an adsorbed hydrogen atom, the latter process, perhaps, being the more likely.



Type A adsorption



An alternative suggestion (2) is that of chemisorption with simultaneous ring cleavage (type B adsorption). This step probably would be rate controlling, in which case the reaction rate should be directly proportional to the cyclopropane pressure; except with platinum, this relationship is not usually observed (12). A step such as this, or the equivalent step for type A adsorption, might conceivably be important in the metal-catalyzed isomerization of cyclopropane to propene in the absence of gaseous hydrogen (51, 115, 127, 154).


Type B adsorption

It also may be possible (12) for cyclopropane to chemisorb by bond formation between delocalized electrons of the ring and the orbitals of the metal surface atoms (type C adsorption). Because of the small amount of delocalization in cyclopropane (for evidence on this point see section II) the bond would be relatively weak compared with that formed by an olefin. Possible reactions of such a species are similar to those for type A adsorption.

Of the three modes of adsorption, only type A has unambiguous supporting evidence. Rather intensive studies seem to be necessary if the various possible steps are to be distinguished.

B. HYDROGENOLYSIS OF CYCLOPROPANE ON METAL OXIDES

On chromia at 50° the cyclopropane–deuterium exchange allows the introduction of one deuterium atom per molecule of cyclopropane, for each period of adsorption of the latter on the catalyst surface (18, 152). The reaction is about fifty times faster than that between cyclohexane and deuterium, and has an activation energy of 7.1 kcal. Above 100° deuterolysis occurs, with an activation energy of 12 kcal.; ring cleavage is thought to involve an interaction of adsorbed cyclopropane species of type A with deuterium to form a diadsorbed propyl radical (18). These reactions have not otherwise been studied.

C. HYDROGENOLYSIS OF ALKYL- AND ARYLCYCLOPROPANES

In general, the effect of ring substituents on these reactions must be considered both with regard to the mode of adsorption of the reactant, and with regard to the transition state of the rate-determining step, *i.e.*, the step involving ring cleavage.

In the gas phase, alkylcyclopropanes react faster than cyclopropane. Thus during their simultaneous hydrogenolysis on platinum–pumice at 100°, methylcyclopropane reacts about 1.2 times faster than cyclopropane. Comparison of the initial rate kinetics of the two reactions shows that methylcyclopropane is the more strongly adsorbed of the two cycloalkanes, and this fact could account for the different rates of hydrogenolysis (12). More recently it has been found that, on supported platinum catalysts at 50° and at a hydrogen/hydrocarbon ratio of about 15, dicyclopropylmethane reacts 1.3 ± 0.1 times faster than butylcyclopropane, and 2.8 ± 0.3 times faster than isobutylcyclopropane. Under similar conditions but with a nickel–kieselguhr catalyst, dicyclopropylmethane reacts about 200 times faster than cyclopropane (19). The latter figure, especially, may constitute evidence for the intervention of a physically adsorbed state as a necessary intermediate for reaction (19).

From other experiments carried out with polyalkylcyclopropanes over nickel–kieselguhr at temperatures of 180° or more and under 130 atm. of hydrogen, it was concluded that an increase in the number of alkyl substituents causes a fall in the reaction rate (82, 83, 137).

However, since the reactions concerned were carried out singly rather than competitively, the conclusion is valid only if each reactant was completely free of any compound that might poison the nickel catalyst. The anomalous product distributions obtained from the hydrogenolysis of 1,1,2-trimethylcyclopropane show that in this case, at least, this condition was not fulfilled.

The influence of alkyl substituents on the position of hydrogenolysis on nickel, palladium and platinum catalysts is shown in Table III. In general the ring cleaves mainly, though not exclusively, in bonds remote from the point of substitution. An increase in the size of the alkyl substituent, as from methyl to isobutyl, has little effect. With a polyalkylcyclopropane the directing influence due to *gem*-dialkyl substituents predominates over that due to a single substituent.

On platinum–pumice at 25° methylcyclopropane opens 95% in the C_2–C_3 position (12). If the products were at thermodynamic equilibrium (119) the figure would be 72%; clearly, the reaction mechanism favors this mode of cleavage. At 125° the observed figure drops to 91%, and the equilibrium figure to 56%. Activation energies for the formation of *n*- and isobutanes are 10.1 and 8.4 kcal., respectively (12).

To some extent the distribution of cleavage depends on rather minor variations in the catalyst preparation. Thus with three platinum–alumina catalysts, the extent of cleavage in the C_2–C_3 bond of isobutylcyclopropane varied from 88 to 96%. In addition, with one particular 5% platinum–alumina catalyst, the mole per cent of 2,4-dimethylpentane formed at complete conversion from the hydrogenolysis of dicyclopropylmethane increased steadily from 72.1 for a catalyst reduced at 280° to 82.4 for one reduced at 650° (19). A catalyst of reduced nickel oxide is especially prone to give irreproducible results (19).

Many of the results listed in Table III are anomalous, in that the main positions of hydrogenolysis are adjacent to the points of substitution. Such results were mostly derived from reactions on supported metal catalysts at temperatures of 150° or more, and are consistent with a mechanism involving isomerization of the alkylcyclopropanes to olefins on the support, followed by hydrogenation of the olefins on the metal. The mechanism implies that a metal may selectively catalyze the reduction of olefins in preference to the hydrogenolysis of alkylcyclopropanes; experiments have shown that this is quite possible (section IIIA). Moreover, in the absence of a metal the conversion of alkylcyclopropanes to olefins is readily brought about by alumina, aluminosilicates, kieselguhr or pumice at temperatures around 150°, and by charcoal at about 220° (32, 104, 106, 107).

The anomalous results reported for the hydrogenolysis of spiropentane on metal powders are incorrect, the reactant having been mistakenly identified (149, 168).

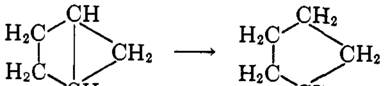
TABLE III

HYDROGENOLYSIS OF ALKYL- AND ARYLCYCLOPROPANES ON METALS

Reactant	Catalyst	Temp., °C.	Hydrogen press. atm.	Distribution of ring cleavage,[a] %			Ref.
				C_1–C_2	C_1–C_3	C_2–C_3	
		Alkylcyclopropanes					
Methylcyclopropane	5% Pt–pumice	15	0.2	2.5	2.5	95	12
Ethylcyclopropane	Ni	*ca.* 100	1	0	0	100	130
	Pt–C	50	1	0	0	100	74, 103
	20% Pt–kiesel.	150	1	42.5	42.5	15	107
Isopropylcyclopropane	Ni–kiesel.	150	85	5	5	90	158
	Pd–C, Pt–C	120	1	0	0	100	78
n-Butylcyclopropane	5% Ni–kiesel.[a]	50	1	6.5	6.5	87	19
	5% Pt–Al_2O_3[b]	50	1	15.5	15.5	69	19
Isobutylcyclopropane	5% Pt–Al_2O_3	50	1	6	6	88	19
Dicyclopropylmethane	5% Pt–Al_2O_3	50	1	9.5	9.5	81	19
1,1-Dimethylcyclopropane	Ni–kiesel.	150	1	50	50	0	150
1,1-Diethylcyclopropane	Ni–kiesel.	180	136	0	0	100	137
Spiro[2,5]octane	Ni–kiesel.	155	129	0	0	100	137
4-Methylspiro[2,5]octane	Ni–kiesel.	155	129	0	0	100	137
1-Methyl-1-isohexylcyclopropane	Pt–C	180	1	0	0	100	79
Spiro[2,2]pentane	PtO_2[c]	20	1	0	0	100	143
1-Methyl-2-isopropylcyclopropane	Ni	100	1	0	Some	Some	92
1,1,2-Trimethylcyclopropane	Ni	100	1	0	0	100	91
	Ni–kiesel.	250	190	18	73	9	82
	20% Pd–C [d]	220	1 (+N_2)	Some	Main	Some	104
	20% Pd–C[e]	260	1	0	0	100	105, 108
	Pt–C	10–150	1	0	0	100	73, 74, 107 108
	20% Pt–kiesel.	150	1	(79)		21	107
1,1-Dimethyl-2-isobutylcyclopropane	Ni	100	1	0	0	100	92
1,1,2,2-Tetramethylcyclopropane	Ni–kiesel.	250	137	9	45.5	45.5	83
Bicyclo[2,1,0]pentane	PtO_2	20	1	100	0	0	27
		Arylcyclopropanes					
Phenylcyclopropane	Pd, Pt	15	1	50	50	0	80
cis- or *trans*-1,2-diphenylcyclopropane	Pd	20	1	100	0	0	81

[a] Figures are for 80–100% conversion except for the cases noted by the superscripts: [a] 29.4, 6.1, [c] 31, [d] 55, [e] 60.

On other occasions a reaction at a *metal* surface may afford an anomalous mode of cleavage. Thus if the geometry of the reactant is such that one bond of the ring is more strained than the others, hydrogenolysis tends to occur in that bond regardless of the positions of alkyl substituents (19). Examples are the conversion of bicyclo[2,1,0]pentane to cyclopentane on platinum oxide at 20° (27) and the hydrogenolysis of bicyclo[2,2,1,$0^{1,7}$]heptane (111).



In addition, if an alkylcyclopropane tends to adsorb at the side-chain rather than at the ring atoms, cleavage may again be anomalous (19). Thus during the hydrogenolysis of dicyclopropylmethane on nickel catalysts at 50°, the main product at complete conversion is 2-methylhexane. This product can result only if the position of cleavage in one ring is different from that in the other ring. The most likely mechanism proceeds *via* the formation of isobutylcyclopropane radicals adsorbed at the side-chain. These radicals then undergo a surface migration so that the point of adsorption shifts along the side-chain, and may eventually involve the ring carbon atoms; initially the ring will adsorb at the substituent-bearing carbon atom, and will therefore cleave mainly in bonds adjacent to this atom (19). With platinum catalysts 2-methylhexane is the main product at 142°, again due probably to surface migration effects, but these are much less important at 50° (19).

On nickel catalysts at 50° alkylcyclopropanes undergo demethanation as well as hydrogenolysis. About 10% of the products of the hydrogenolysis of dicyclopropylmethane, for example, consist of hexane, propylcyclopropane, 2-methylpentane and pentane. Since alkanes are not hydrogenolyzed under these conditions (16) the demethanation must accompany ring cleavage (19). *n*-Butylcyclopropane gives substantial amounts of hexane but little or no pentane, showing that the process favors the separation of a CH_2 group rather than a CHR group (19). If an alkylcyclopropane is initially adsorbed at the side-chain, and then undergoes ring cleavage *via* migration of the position of adsorption from the side-chain to the ring, demethanation does not occur. Since the extent of demethanation during the hydrogenolysis of dicyclopropylmethane on nickel–kieselguhr decreases with time, the process may require sites with a particular geometry (19).

The means by which an alkyl substituent exerts a directing influence on hydrogenolysis is uncertain. Consider the situation for a monoalkylcyclopropane, taking each of the possible modes of adsorption (section IIIA) in turn. It is assumed that free radical intermediates are unlikely.

With type B adsorption, involving simultaneous ring cleavage, the directing influence might arise from a steric repulsion between the alkyl substituent and the metal surface; this would hinder the formation of a carbon–metal bond at the substituent-bearing carbon atom, and thereby inhibit cleavage at adjacent carbon–carbon bonds.

Type A adsorption requires cleavage of a carbon–hydrogen bond. If this occurs mainly at the secondary ring carbon atoms, then steric hindrance can again account for the position of ring cleavage. It is conceivable, though, that an alkyl substituent favors adsorption at the tertiary carbon atom (19), in which case the mode of cleavage must be attributed to the operation of some form of electronic effect on the transition state. Generally speaking, polarization effects due to alkyl substituents should be small in cases of homolytic cleavage, but this is not always the case for homogeneous reactions (98), and so predictions regarding heterogeneous reactions must be rather tentative.

Adsorption at the alkyl side-chain favors ring cleavage at bonds adjacent to the substituent-bearing carbon atom. Since the replacement of a methyl substituent by *n*-butyl has little effect on the distribution of ring cleavage (Table III), such adsorption must be relatively unimportant.

Should type C adsorption arise, the directing influence of an alkyl substituent might again be due mainly to steric hindrance; an inductive effect operating so as to withdraw electrons from the alkyl group could also be responsible (12), although this is not very likely should the cleavage be purely homolytic. Similar electron-releasing effects govern the electrophilic reactions of alkylcyclopropanes, as in the addition of hydrogen bromide to methylcyclopropane to give 2-bromobutane (44, 96, 134).

The behavior of arylcyclopropanes on hydrogenolysis shows interesting differences from that of alkylcyclopropanes. Hydrogenolysis of phenylcyclopropane at 20° on platinum or palladium catalysts yields *n*-propylbenzene; the reaction on platinum also yields small amounts of cyclohexane derivatives (80). On rhodium–alumina, phenylcyclopropane reacts faster than cyclopropane (8). On palladium at 20°, the rates of hydrogenolysis of diphenylcyclopropanes fall in the order: *trans*-1,2-diphenylcyclopropane > phenylcyclopropane > *cis*-1,2-diphenylcyclopropane > 1,1-diphenylcyclopropane; the latter derivative does not react, but the 1,2-diphenylcyclopropanes open at the C_1–C_2 bond (81).

Initially phenylcyclopropane might adsorb at either of the two rings. If it adsorbs mainly at the cyclopropyl ring, then the phenyl ring might be expected to hinder sterically cleavage of bonds adjacent to the tertiary carbon atom, in the manner discussed for

TABLE IV

HYDROGENOLYSIS OF ALKENYLCYCLOPROPANES

Reactant	Catalyst	Temp., °C.	Hydrogen press., atm.	Distribution of ring cleavage,[a] % C_1–C_2	C_1–C_3	C_2–C_3	References
Methylenecyclopropane	Pt–pumice	15	0.4	39	39	22	13
	Pt–pumice	100	0.4	45	45	10	13
	Copper chromite	110	95	50	50	0	42
Vinylcyclopropane	Raney Ni	20	4.4	50	50	0	159
	Pt, Pd	120	1	50	50	0	79
Isopropenylcyclopropane	Raney Ni	60	68	47	47	5	158
	Pd	120	1	50	50	0	75, 78
	Pt	15	1	50	50	0	76, 78
	Copper chromite	100	102	50	50	0	145, 148
Isopropylidenecyclopropane	Ni	160	1	50	50	0	167
2-Cyclopropylbutene-1[b]	Copper chromite	100	102	50	50	0	147, 148
2-Cyclopropylbutene-2[c]	Copper chromite	100	102	50	50	0	147, 148
4-Methyl-1-(1′-methylcyclopropyl)-pentene-1	Pd	15	1	50	50	0	79
2-Phenylvinylcyclopropane[d]	Pd	20	1	50	50	0	135

[a] The reactions proceeding *via* alkylcyclopropanes are ignored. [b] Similar results are found with 2-cyclopropylpentene-1 and 2-cyclopropylhexene-1. [c] Similar results are found with 2-cyclopropylpentene-2 and 2-cyclopropylhexene-2. [d] In this case the reaction product is an olefin.

alkylcyclopropanes. Actually, such influences appear to be insignificant; this point is especially emphasized by the relatively high rate of hydrogenolysis of *trans*-1,2-diphenylcyclopropane. The most likely explanation of the results is that based on the action of polarization effects on the transition state. It is quite possible that such effects will be stronger with arylcyclopropanes than with alkylcyclopropanes, due to the unsaturated nature of the phenyl ring (19). In accordance with this suggestion, the fall in the rates of hydrogenolysis of the arylcyclopropanes parallels a decrease in conjugation in the reactants as judged from the intensity of the Raman spectra (5).

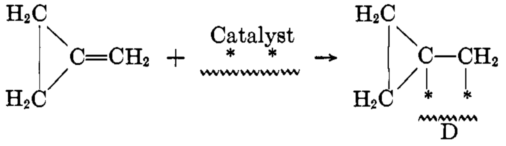
There remains the additional possibility that phenylcyclopropane (for example) adsorbs initially at the phenyl group, and that ring cleavage occurs by way of a migration of the position of adsorption to the cyclopropyl ring. Judging from the fact that the benzene–deuterium exchange on palladium is inhibited by cyclohexane (7), this mode of adsorption does not seem too likely.

D. HYDROGENOLYSIS OF ALKENYLCYCLOPROPANES

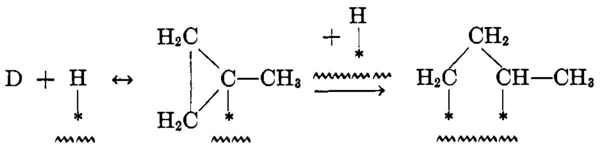
Alkenylcyclopropanes undergo ring cleavage mainly at bonds adjacent to the point of substitution; thus these reactions do not necessarily involve the formation of the corresponding alkylcyclopropanes. The relevant literature is summarized in Table IV; copper chromite is considered to behave as a metal catalyst, although this is not yet certain.

The only reaction to have been studied in detail is the hydrogenolysis of methylenecyclopropane on platinum–pumice (13). Initial rate kinetics indicate that methylenecyclopropane achieves a higher surface coverage than either hydrogen or isobutene. The activation energy for the reaction (17.4 ± 2.0 kcal.) is about 15 kcal. larger than that for the hydrogenation of isobutene. At 17° the reaction gives methylcyclopropane, butane and isobutane in the ratios 6:2.5:1; hydrogenolysis of methylcyclopropane becomes appreciable only beyond 60% conversion of the olefin. At 100° the four butenes are also formed, while the relative rate of formation of methylcyclopropane is halved; initially the concentration of butene-1 appreciably exceeds its equilibrium value, but the difference diminishes as the reaction proceeds due to isomerization to *cis*- and *trans*-butene-2. The rate of removal of the butenes is only one-tenth that of methylenecyclopropane, and only one-half that of methylcyclopropane under similar conditions at 17°. The amounts of branched hydrocarbons formed decrease with increasing temperature.

The most likely mechanism for this reaction proceeds *via* chemisorption of the olefin at the double bond in the manner (13)



The four carbon atoms of species D are in a plane parallel to the metal surface. The adsorption step is probably accompanied by a change in hybridization of the bonding orbitals of atoms C_1 and C_4 from sp^2 to sp^3, so that the adsorbed state is stabilized by a decrease in ring strain at atom C_1. This suggestion is consistent with the higher surface coverage and faster reaction achieved by methylenecyclopropane with respect to the butenes. The reactions of species D with adsorbed hydrogen atoms can either give methylcyclopropane or lead to ring cleavage by steps such as



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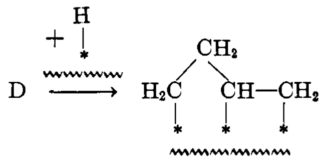
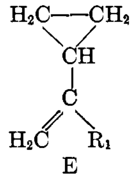


Branched chain hydrocarbons can only result from attack at a methylenic ring carbon atom (13).

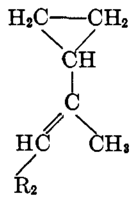
An alternative mechanism has been proposed, in which the olefin interacts with adsorbed hydride ion to form a carbanion–metal complex that either adds on a proton to give the corresponding alkylcyclopropane, or undergoes ring cleavage. The directing effect of ring substituents is attributed to their effect on the stabilities of the anions formed during ring cleavage (157). While this latter suggestion may be partly correct should the adsorbed olefin have some carbanion character, the mechanism as a whole is improbable. The bonding of hydrogen atoms to the surface of a transition metal, for example, is mainly covalent (35, 118), there being little evidence for the existence of adsorbed hydride ions.

An increase in the number of carbon atoms joining the cyclopropyl ring to the double bond does not alter the main position of ring cleavage, but it does appear to reduce the rate, although this conclusion is based on studies with a number of catalysts and may be in error (158, 159). These observations may be reasonably interpreted in terms of a mechanism involving an initial chemisorption at the double bond, a subsequent migration of the position of adsorption to the ring, and ring cleavage. As the number of carbon atoms linking the double bond and the ring increases, the chance that the surface migration will lead to adsorption at the ring must decrease markedly, since the migration is entirely random in direction. Thus a corresponding decrease in the rate of hydrogenolysis is not unexpected.

Similar considerations may explain certain features of the hydrogenolysis of 2-cyclopropylalkenes on a catalyst of copper chromite promoted with barium oxide. The reactants fall into two groups, namely, 1-alkenes of structure E with R_1 as methyl, ethyl, *n*-propyl, or *n*-butyl, and 2-alkenes of structure F with R_2 as methyl, ethyl or *n*-propyl; the 2-alkenes are mixtures of geometrical isomers (147, 148). Hydrogenolysis affords the corresponding alkylcyclopropanes, which are non-reactive, together with smaller amounts of alkanes formed from ring cleavage in bonds adjacent to the tertiary carbon atom. The double bond of the 1-alkenes is reduced about 16 times faster than that of the 2-alkenes, yet the latter suffer 16 times as much ring cleavage (147, 148). Two influences may be important here. The introduction of the third alkyl group adjacent to the double bond may sterically hinder adsorption at that bond, and after adsorption it may hinder attacks by adsorbed hydrogen atoms. Both influences would favor adsorption at the ring carbon atoms, the preliminary step to ring cleavage, by hindering the competitive steps.



E

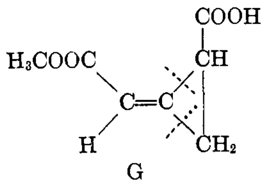


F

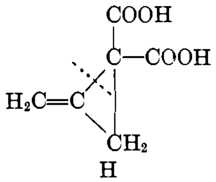
E. HYDROGENOLYSIS OF OTHER CYCLOPROPANE DERIVATIVES

Carbon groups readily interact with metal surfaces (22, 151). If, therefore, such a group is a substituent in a three-membered carbon ring, it may be expected to behave similarly to a carbon–carbon double bond by facilitating cleavage in bonds adjacent to the substituent-bearing carbon atom. The hydrogenolysis of methylcyclopropylketone to 2-pentanone on Raney nickel (146) or copper (38) and of diethyl-2-formylcyclopropane-1,1-dicarboxylate to γ,γ-dicarbethoxybutyraldehyde on palladium (161) both constitute evidence supporting this mechanism.

Similar effects appear in the hydrogenolysis of carboxylic acids and esters of alkenylcyclopropanes, of which a rather detailed review is available (157). The reactions were carried out in the liquid phase on platinum oxide or palladium–charcoal at 20–30° (87, 88, 113, 129, 157, 162, 163). The introduction of carboxyl ring substituents facilitates hydrogenolysis (157). Usually the ring opens at a bond adjacent to the side-chain containing the carbon–carbon double bond, but the presence of carboxyl substituents at one of the other ring carbon atoms tends to limit cleavage to that bond linking the substituent-bearing carbon atoms. Thus the main positions of cleavage in derivatives G and H are those shown by the broken lines; similar observations have been made with derivatives of vinylcyclopropane (157). While these effects may arise from the chemisorption of the molecules at the carboxyl groups, the additional possibility that polarization phenomena influence the transition states (157) cannot be ruled out.

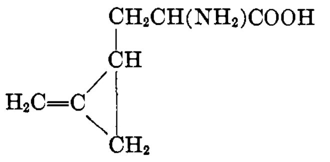


G



H

Hydrogenolysis of 1-aminocyclopropane-1-carboxylic acid occurs to a similar extent at all three positions in the ring (14); this is also the case for hypoglycine A (species J) (49), when reduced *via* the corresponding alkyl derivative (157). If the latter reaction does



J

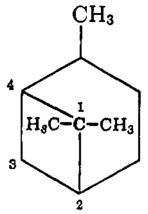
not involve the alkyl derivative, however, the ring cleaves at a bond adjacent to the carbon–carbon double bond (129).

IV. HYDROGENOLYSIS OF FOUR-MEMBERED CARBON RINGS

Cyclobutane and its derivatives require much more strenuous conditions for hydrogenolysis than do the corresponding cyclopropanes (103, 164, 165), while cyclopentanes are less reactive still. This series parallels the increase in the carbon–carbon bond energies (section II).

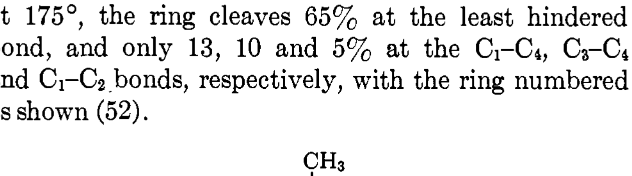
The modes of hydrogenolysis of several alkylcyclobutanes have been studied (Table V), mainly by Kazanskiĭ, Lukina and co-workers. With the reactions on palladium and platinum catalysts at about 250°, substituent effects are relatively small. Thus the 1,3-dialkylcyclobutanes cleave just as fast as the monoalkyl derivatives (72), and even the isomers of 1,3-dimethyl-2,4-diphenylcyclobutane cleave quite readily on platinum–alumina at 235° (117). Moreover, methyl and ethyl substituents do not appreciably influence the relative rates of cleavage at different carbon–carbon bonds (72, 74, 103, 105). An isopropyl substituent, however, inhibits cleavage at adjacent bonds, probably due to steric repulsion between the substituent and the catalyst surface.

A few studies have been carried out with nickel catalysts. The ethylcyclobutane–deuterium exchange on a nickel film at 150° gives ethylcyclobutanes-d_1. . . d_{12}; rather weak maxima occur at the mono- and decadeuterio derivatives. The exchange is accompanied by a small amount of deuterolysis (133). Methylcyclobutane is reported to hydrogenolyze on nickel to isopentane (131), but this now seems doubtful in view of the contrasting results obtained with platinum catalysts. Larger substituents, though, do exert appreciable effects. Thus in the hydrogenolysis of the four-membered ring of pinane on nickel–kieselguhr at 175°, the ring cleaves 65% at the least hindered bond, and only 13, 10 and 5% at the C_1–C_4, C_3–C_4 and C_1–C_2 bonds, respectively, with the ring numbered as shown (52).



On chromia, ethylcyclobutane exchanges with deuterium about 5.3 times faster than cyclohexane, but only about 0.11 times as fast as cyclopropane (152). The relative rates of exchange parallel the acidities of the carbon–hydrogen bonds. Deuterolysis of ethylcyclobutane occurs at 200° (152).

The mechanism of hydrogenolysis of an alkylcyclobutane probably involves the formation of adsorbed radicals by steps such as



Ring cleavage may require the interaction of such radicals with adsorbed hydrogen. The weak directing effects of alkyl substituents on these reactions contrast markedly with those found for the hydrogenolysis of alkylcyclopropanes at lower temperatures (section IIIC); the following points seem important here.

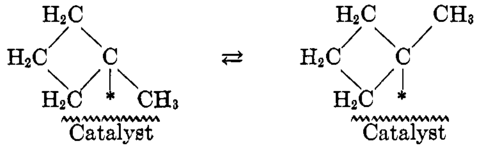
First, it seems reasonable to suppose that the relative rates of isotopic exchange of cyclopropane, ethylcyclobutane and cyclohexane on metals will be similar to those noted above for a chromia catalyst. If this is correct, then the adsorption and subsequent surface migration of an alkylcyclobutane will involve the carbon atoms of the side-chain to a much greater extent than will the corresponding processes for an

TABLE V

HYDROGENOLYSIS OF FOUR-MEMBERED CARBON RINGS

Reactant	Catalyst	Temp., °C.	Hydrogen press., atm.	Distribution of ring cleavage, %		References
				C_1–C_2	C_2–C_3	
		Alkylcyclobutanes				
Methylcyclobutane	Ni	210	1	0	100	131
	Pt-C	250	1	50	50	74, 103
Ethylcyclobutane	Pt-C	250	1	50	50	72, 74
	Pd-C	260	1	40	60	105
Isopropylcyclobutane	Pt-C	250	1	30	70	77
		Alkenylcyclobutanes				
Methylenecyclobutane	Pt-pumice	100	0.13	1	99	13
		200	.13	62	38	13
		300	.13	87	13	13

alkylcyclopropane. Further, while the hydrogenolysis of cyclopropane on metals above 0° is faster than isotopic exchange (section IIIA), the reverse relationship appears to hold for ethylcyclobutane on nickel at 150° (133), and may also hold on platinum and palladium at higher temperatures, since hydrogenolysis proceeds rather faster on nickel than on the other metals. Finally, isomerizations such as

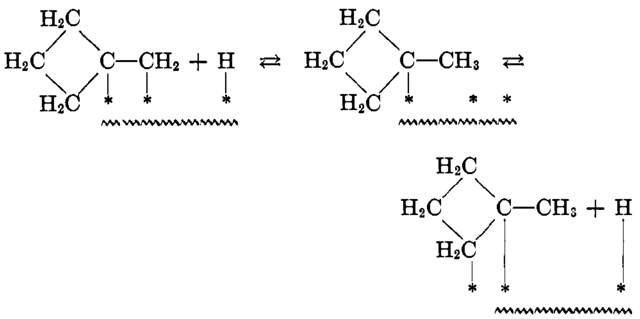


may well be facilitated by high temperatures and also, perhaps, by an increase in ring size from 3 to 4 atoms (128); they may therefore be much faster during the hydrogenolysis of an alkylcyclobutane than during the hydrogenolysis of an alkylcyclopropane.

Such considerations go some way toward explaining different steric effects in these reactions.

The hydrogenolysis of methylenecyclobutane has been examined on platinum–pumice at 50–300° (13). Initial rate kinetics indicate that at 100° the reactants occupy approximately equal parts of the catalyst surface. Below 250° the main product is methylcyclobutane, but ring cleavage occurs at temperatures as low as 100°, giving mainly 2-methylbutene-2. At higher temperatures pentene-1 and *trans*-pentene-2 become important. At 300° olefins constitute about 60% of the products; the ratio of normal/branched olefins is then about 20. At the same temperature appreciable amounts of an isomer of methylenecyclobutane are formed, especially during the early stages of the reaction. The same isomer is formed in the absence of hydrogen, and is probably 1-methylcyclobutene-1.

The reaction probably proceeds in a similar manner to the hydrogenolysis of methylenecyclopropane (section IIID). Isomerization to 1-methylcyclobutene-1 can be visualized in terms of the equilibria



Isopropenylcyclobutane, on hydrogenolysis on platinum–charcoal at 250°, gives the same products as isopropylcyclobutane (77).

V. HYDROGENOLYSIS OF FIVE-MEMBERED CARBON RINGS

The isotopic exchange reactions of cyclopentane and its derivatives at temperatures too low for hydrogenolysis are of considerable interest, and will be briefly surveyed (for detailed reviews see (15, 84)). After one period of adsorption on a nickel, palladium, or platinum surface at temperatures just high enough for exchange (at about 0°), cyclopentane gives mainly cyclopentanes-d_5 and -d_{10}; at higher temperatures cyclopentane-d_{10} predominates (6, 17, 133). The five hydrogen atoms initially exchanged at the lower temperatures can only be those of one face of the ring; an interconversion of monoadsorbed and eclipsed diadsorbed species of cyclopentane accounts for the exchange (17). The hydrogen atoms of alkyl substituents likewise readily exchange, except when isolated by a quaternary carbon atom (17, 133).

The step allowing the exchange of the remaining hydrogen atoms of the ring during the same period of adsorption is uncertain. Recent studies with polymethylcyclopentanes on palladium led to the suggestion that an α,β,γ-triadsorbed radical is a necessary intermediate (128). The strain in the latter is thought to enable the carbon atoms to change from sp^3 to sp^2 hybridization, while forming π-bonds with the catalyst surface; exchange might then occur through an interaction of residual p-orbitals with gas phase or physically adsorbed molecules of deuterium (128). An intermediate of this type also accounts for the *cis–trans* isomerization of 1,1,3,4-tetramethylcyclopentanes on palladium at 80° (128).

The hydrogenolysis of a five-membered ring commonly requires temperatures above 200°. Both the minimum reaction temperature and the reaction products vary considerably on different metals. Platinum is notable in favoring products of relatively simple composition, and so these reactions will be discussed first.

The hydrogenolysis of cyclopentane on platinum–charcoal at 250–300° affords *n*-pentane (65, 169). The reaction has an activation energy of 35 kcal. (61), and is inhibited by increasing hydrogen pressure (41, 71), indicating a competitive adsorption of the two reactants at the catalyst surface. On platinum–alumina catalysts at temperatures above 350° the reaction is more complex, and gives methane and aromatic hydrocarbons (47, 116, 138). Ring cleavage also occurs on passing a cyclopentane–cyclohexane mixture in an inert gas over platinum–charcoal at 300° (67), the cyclohexane being dehydrogenated.

The substituent effects in these reactions have been studied in some detail, notably by Kazanskiĭ and coworkers. On platinum–charcoal catalysts the rates of hydrogenolysis of cyclopentane and its methyl, 1,1-dimethyl, *trans*-1,2-dimethyl and *trans*-1,3-dimethyl derivatives fall in the ratios 11.7:7:7.5:2:1 (57, 63); with the 1,2,3-trimethylcyclopentanes isomerization is much faster than hydrogenolysis (69). On platinum–alumina catalysts at 330°, four or more methyl substituents prevent hydrogenolysis of the ring until after the occurrence of demethanation (41).

The ring cleaves mainly at bonds remote from the points of substitution (Table VI). On platinum–charcoal at 320°, for instance, methylcyclopentane cleaves only 11% in bonds adjacent to the substituent-bearing carbon atom (62), and the figure for 1,1-dimethylcyclopentane is close to zero (64). On 20% platinum–alumina catalysts at 315°, and under 30 atm. hydrogen, methylcyclopentane gives a figure of 6%, but this decreases almost to zero at low conversions (41).

The effects of changes in the metal content of platinum–alumina catalysts on the product distributions are reported for the hydrogenolysis of methylcyclopentane, and of 1,3-dimethylcyclopentane, at 330° (40, 41). While a decrease in the platinum concentration from 20 to 2% has relatively little effect, further reductions cause notable increases in the extent of cleavage in bonds adjacent to the substituent-bearing carbon atoms (41). The relations between the product distributions and the other experimental variables also change at low platinum concentrations. It is not clear how these phenomena arise. An increased participation of reactions on the support might be mainly responsible, but other considerations, such as that of large changes in the electron band structure of the platinum crystallites (see for example (124)), may also be important. Another interpretation is based on different types of close packing of chemisorbed alkylcyclopentanes on large and small platinum crystallites (41), but such close packing seems unlikely to exist at 330°.

The product distributions for the reactions on platinum–charcoal catalysts may be reproduced quite well from empirical calculations (120, 121). Suppose that an alkylcyclopentane chemisorbs initially by the separation of a hydrogen atom and the formation of a carbon–metal bond, and that repetition of this process at a ring carbon atom adjacent to that already adsorbed leads to stretching, and ultimately to cleavage, of the carbon–carbon bond. Then the extent of cleavage at any particular carbon–carbon bond is proportional to one-half the number of hydrogen atoms bonded to the two carbon atoms. On this basis methylcyclopentane should cleave 22% at bonds adjacent to the tertiary carbon atom. This value is about twice that found experimentally (62), but the discrepancy may be corrected by assuming that the ring cleaves at bonds adjacent to the tertiary carbon atom only after initially adsorbing at that atom. Agreement between calculated and observed distributions is then close for methyl- and 1,1-dimethylcyclopentanes, and is qualitative for the 1,2- and 1,3-dimethylcyclopentanes.

The treatment is probably correct in stressing the relation between the mode of ring cleavage and the distribution of hydrogen atoms bonded to the ring carbon atoms. The validity of the initial assumptions is less certain, since similar calculations can be made from entirely different assumptions, and with about the same degree of success.

It is curious that methyl substituents exert quite a definite influence in these reactions, yet appear to have little effect on the hydrogenolysis of a cyclobutyl ring (section IV); however, this may arise merely from the lack of accurate results for methylcyclobutane.

Ethyl and isopropyl substituents exert directing effects similar to that of the methyl group, yet *n*-propyl, by comparison, favors hydrogenolysis at bonds adjacent to the point of substitution (Table VI). Increased adsorption at the side-chain could account for this, but similar effects would then be expected for the other substituents. Derivatives higher than methylcyclopentane undergo substantial demethanation, and in addition the butylcyclopentanes and higher homologs yield aromatic hydrocarbons (120). If the latter are formed by way of an expansion of the five-membered carbon ring, then presumably methyl- and ethylcyclopentanes would react in this manner; this is not

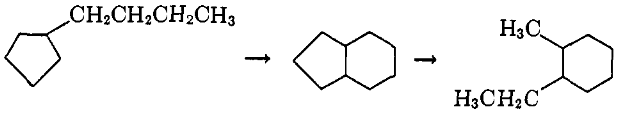
TABLE VI

HYDROGENOLYSIS OF ALKYLCYCLOPENTANES ON PLATINUM CATALYSTS

Cyclopentane derivative	Catalyst	Temp., °C.	Hydrogen press., atm.	Distribution of ring cleavage,[a] %					Ref.
				C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_1	
Methyl	20% Pt–Al_2O_3	315	30	2.8	31.4	31.4	31.4	2.8	40, 41
Methyl	10% Pt–C	320	1	5	32	26	32	5	62
Ethyl[b,c]	10% Pt–C	300	1	3	(	94	)	3	60
n-Propyl[b]	10% Pt–C	300	1	16.5	28	11	28	16.5	60, 170
1,1-Dimethyl	20% Pt–C	300	1	0	37	26	37	0	64
trans-1,2-Dimethyl[b]	20% Pt–C	300	1	5	5	42.5	42.5	5	57, 63
1,3-Dimethyl	10% Pt–Al_2O_3	330	30	15	15	15.5	39	15.5	40, 41
trans-1,3-Dimethyl	20% Pt–C	305	1	14.2	14.2	14.2	45	14.2	57, 63
1,2,3-Trimethyl (any isomer)	20% Pt–C	303	1	0	0	0	100	0	69

[a] Less detailed information is available for isopropyl- (70), *n*-butyl- (58), isoamyl- (59, 142), 1-methyl-1-ethyl- (86, 114) and 1-methyl-1-*n*-propylcyclopentanes (86, 114), and for bicyclo[2,2,1]heptane (66). [b] Analysis of the products is incomplete. [c] Substantial amounts (10–25%) of low-boiling alkanes are also formed.

observed, possibly because of the ineffective analytical methods then used. However, it could also be that six-membered rings are formed by closure of the side chain, giving a hydrindane which suffers dehydrogenation with cleavage of the five-membered ring, thus (58)



The observation of dialkyl- as well as monoalkylbenzene derivatives among the reaction products supports such a process (58). On the other hand, the conversion of 1-methyl-1-ethylcyclopentane on platinum–charcoal at 320° to ethylbenzene and xylenes to the extent of 28 and 12%, respectively (86), can only be explained in terms of ring expansion.

The reactions of several phenylcyclopentanes with hydrogen have also been studied. On platinum–charcoal catalysts at 300°, phenylcyclopentane, phenylcyclopentylmethane, 1-phenyl-2-cyclopentylethane and 1-phenyl-3-cyclopentylpropane all give alkylbenzenes as the main products. Phenylcyclopentane cleaves at all three positions and reacts faster than cyclopentane (28). Under similar conditions the derivatives 1-phenyl-4-cyclopentylbutane, 1-phenyl-5-cyclopentylpentane and 1-phenyl-6-cyclopentylhexane cnly undergo hydrogenation of the phenyl rings (29, 30, 31).

The reactions of cyclopentane derivatives with hydrogen on palladium catalysts proceed quite differently. Attempts to hydrogenolyze cyclopentane on palladium–charcoal at 330° failed, even at elevated pressures of hydrogen (68). Alkylcyclopentanes isomerize to six-membered rings under these conditions, but yield little or no alkanes (109, 110). The marked differences in behavior of platinum and palladium catalysts remain unexplained.

On nickel catalysts ring opening is accompanied by extensive cleavage of carbon–carbon bonds. Cyclopentane, for example, cleaves at about 200° to give methane, *n*-pentane, and traces of aromatic hydrocarbons (68, 71, 141); the methane could result either from cyclopentane or from *n*-pentane. Thus nickel at 200° behaves similarly to platinum–alumina catalysts at 400°. Hydrogenolysis of methylcyclopentane on nickel–alumina at 240° gives 2- and 3-methylpentane, low boiling alkanes, and aromatic hydrocarbons (62, 112). In contrast, the same reactants on nickel–silica–alumina at 280° and 24.8 atm. hydrogen give mainly cyclohexane (21), probably due to the catalytic activity of the silica–alumina. Hydrogenolysis of bicyclopentyl gives only cyclopentane derivatives, showing that ring cleavage is favored by a particular orientation of the ring to the surface (140, 141).

Studies with Raney nickel catalysts at 200° show that initially an alkylcyclopentane undergoes a simple ring cleavage to an isoalkane; the latter then suffers successive demethylations, mainly at the expense of those carbon atoms which previously formed part of the five-membered ring. Ethylcyclopentane, for instance, gives 3-methylpentane but no 2-methylpentane. No normal alkanes appear to be formed (141). It seems that the reactions on nickel proceed similarly to those on platinum except in that they promote a greatly increased fragmentation of the products, due, perhaps, to the formation of stronger carbon–metal bonds.

Hydrogenolysis of indan on nickel–kieselguhr at 50° and 100 atm. hydrogen gives mainly dialkylcyclohexanes; hexahydroindan may be a reaction intermediate (53). On copper–alumina at 325°, the reaction gives 60% aromatic hydrocarbons; hexahydroindan under these conditions hydrogenolyzes to a complex mixture of products, six-membered rings being predominant (53).

The hydrogenolysis of 1-butylcyclopentene-1 on Raney nickel at 200° gives the same products as the hydrogenolysis of butylcyclopentane; similarly, isoamylcyclopentene-1 and isoamylcyclopentane give identical products (139). Apparently the presence of the double bond does not lower the temperature required for ring cleavage.

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