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Hydrogenolysis of Alkanes with Quaternary Carbon Atoms over Pt and Ni Black Catalysts

By HELGA ZIMMER, PÁL TÉTÉNYI AND ZOLTÁN PAÁL*

Institute of Isotopes of the Hungarian Academy of Sciences, H-1525 Budapest,
P.O. Box 77, Hungary

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Hydrogenolysis of hydrocarbons with quarternary C atoms (neopentane, neohexane, 2,2,3-trimethylbutane, 2,2- and 3,3-dimethylpentanes and 2,2,3,3-tetramethylbutane) has been studied over Pt and Ni black catalysts. The reactivities of different types of C—C bond have been determined. The probability of C—C bond rupture where one of the carbon atoms is quaternary is inversely proportional to the bond dissociation energy. On Pt, two essential types of hydrogenolysis can be distinguished. One reaction is responsible for the breaking of internal C—C bonds attached to the quaternary carbon atom and the other for demethylation. With larger molecules, the former reaction is preferred and the surface intermediate should be 1,4-diadsorbed, while that for the latter reaction is 1,3-diadsorbed. Nickel, as previously suggested, causes terminal C—C rupture, although with branched hydrocarbon reactants internal C—C bond rupture is also possible, presumably *via* 1,4-adsorption.

General features of hydrogenolytic reactions depending on the nature of the metal catalyst have been observed and summarized by various authors.[1-4] Three formal characteristics, the activity of the metal and the depth and pattern of hydrogenolysis, have been proposed as being sufficient to describe this reaction.[4] An optimum adsorption strength is needed for maximum catalytic activity; neither too strong nor too weak metal–hydrocarbon interaction favours the formation of the intermediates involved in hydrogenolysis.[5] As far as the depth of hydrogenolysis is concerned, two different sorts of behaviour have been observed:[3] single bond rupture over Pt, Pd, Rh and Ir and deep fragmentation (multiple rupture) over other Group VIII metals. Deep fragmentation over Ni has been attributed to demethylation.[6] Ponec and coworkers[7] defined a factor enabling them to distinguish between terminal C—C rupture and 'true' multiple fragmentation. The demethylating character of nickel has been confirmed by studies with n-butane which, in the presence of an excess of hydrogen, undergoes almost random single bond rupture on platinum.[8]

Leclercq *et al.*[9, 10] studied extensively the hydrogenolysis of various hydrocarbons over a Pt–Al_2O_3 catalyst. They defined a 'reactivity factor' ω to characterize the pattern of hydrogenolysis

$$\omega = \frac{\text{actual rate of rupture}}{\text{statistical rate of rupture}}.$$

The ω factors for all hexane isomers were determined for single hydrogenolysing metals (Pt, Pd, Rh and Ir). Internal rupture was more characteristic of Pt and Ir; thus, taking into account the terminal C—C rupturing character of Ni, the position of preferred rupture was shifted towards internal C—C bonds with metal catalysts in the lower rows of the Periodic Table.[11] Montarnal and Martino[12] attributed this behaviour to the increasing 'softness' of the metal in terms of Pearson's concept of acidity.

The pattern of hydrogenolysis depends on the structure of the hydrocarbon reactant.[9-11] Leclercq *et al.*[9] arrived at the conclusion that the relatively small but consistent variations of hydrogenolysis patterns on Pt as a function of the structure of hydrocarbons can be explained by assuming various possible intermediates for hydrogenolysis, such as 1,2-, 1,3-, 1,4- and 1,5-diadsorbed species.

The structure of the molecule has less influence on the activity of hydrogenolysis. Tétényi[13] found that propane underwent hydrogenolysis with a higher rate and a lower energy of activation than ethane over several metals. This effect was attributed to the possibility of 1,2,3-interactions between the propane molecule and the catalyst. The fact that hydrogenolytic properties of neopentane are closer to those of ethane than to those of propane indicates that 1,3-interaction must be less favourable for the rupture of this molecule. Whereas the rate of C—C bond rupture in ethane showed differences as large as 5-6 orders of magnitude over several Group VIII metals, the differences in activities of the same metals for 3-methylpentane hydrogenolysis was much less: *ca.* 2 orders of magnitude.[13] All these observations point to the importance of three carbon atoms interacting with the catalyst surface (most likely *via* multiple C—M bonds[1]) whereas the rest of the molecule exhibits compensating, directing and other effects of secondary importance.

Attention has to be paid to the influence of hydrogen on the catalytic reaction. The rate of skeletal rearrangement reactions (cyclization and isomerization) has been found to have a maximum as a function of the hydrogen pressure[14] as has also been observed for hydrogenolysis.[8, 15] This was attributed to the hydrogen regulating the concentration of surface intermediates of different degrees of dissociation for each reaction.[16] Working with fixed hydrogen and hydrocarbon partial pressures has the disadvantage that one cannot be sure on which side of the optimum the reaction takes place. Therefore comparison of the reaction rates (or even of the activation energies[17]) includes an element of uncertainty. This may be why we find such discrepancies in the literature regarding the order with respect to hydrogen: negative for the hydrogenolysis of ethane[18, 19] and pentane,[20] positive for n-heptane,[21] isoheptanes,[22, 23] butane and isopentane[20] and a change from positive to negative with maxima for propane, isobutane and neopentane.[20]

The study of compounds containing quaternary carbon atoms has the advantage that some mechanisms can be excluded because certain types of adsorption (for instance 1,2- and 1,3-diadsorbed species) are sterically hindered or impossible. Leclercq *et al.*[9, 10] concluded, on the basis of the reactivity of 2,2,3,3-tetramethylbutane, that in these cases 1,4-diadsorption could become predominant.

In the present work we report a study carried out using hydrocarbons with quaternary carbon atoms (neopentane, neohexane, 2,2,3-trimethylbutane, 2,2- and 3,3-dimethylpentanes and 2,2,3,3-tetramethylbutane) in order to gain a deeper understanding of the nature of hydrogenolytic processes. A comparison of Pt and Ni blacks seemed to be reasonable in order to elucidate the question of whether nickel, which selectively cleaves terminal C—C bonds, is also able to cleave internal C—C bonds attached to the quaternary carbon atom. In the case of such hydrocarbons very pronounced structural effects can be expected, whereas with other hexane[11, 13] and heptane isomers the above-mentioned compensating effect of the rest of the large molecule (not interacting with the surface) may mask primary structural effects.

EXPERIMENTAL

The experiments were carried out in a static circulating apparatus described earlier,[24] connected to a gas chromatograph with a Squalane capillary column. Reaction mixtures contained 1.23 kPa hydrocarbon and 2-60 kPa hydrogen. Platinum black catalyst was precipitated from H_2PtCl_6 at 275 K with HCHO in the presence of KOH[25] and pretreated with hydrogen at 630 K.[26] Its surface area was *ca.* 1.8 m^2 g^{-1} (measured by H_2 adsorption using the B.E.T. method) and its mean crystallite diameter was *ca.* 30 nm (measured by X-ray diffraction). Nickel black catalyst was prepared from $Ni(OH)_2$ and reduced with hydrogen *in situ.*[27] Its specific surface area was *ca.* 4 m^2 g^{-1} and crystallite size *ca.* 15 nm.

The catalyst samples (0.10 g Pt black and 0.34 g Ni black) were regenerated before each experiment in air and hydrogen in the case of Pt and in hydrogen in the case of Ni at the reaction temperature, which was 600 K for Pt and 500 K for Ni.

Hydrocarbons were Merck, Fluka or EGA products, with a purity > 99.5%. Oxygen was removed from them before use by subsequent cooling and outgassing at liquid-nitrogen temperature.

Initial reaction rates were determined from analyses of samples taken after 5 min contact time. Plots of conversion against time justified this approach.

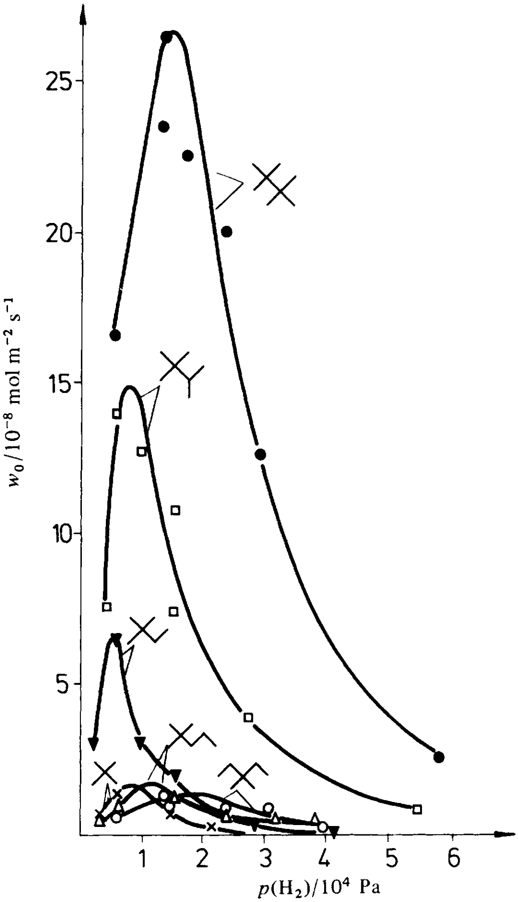


FIG. 1.—Initial rate of rupture of the bond between the quaternary carbon atom and its most substituted neighbouring carbon atom as a function of hydrogen pressure. 0.10 g Pt black catalyst, $T = 603$ K, $p(HC) = 1.23$ kPa.

RESULTS

The initial reaction rates (w_0) for hydrogenolysis of the C—C bonds between the quaternary carbon atom and its most substituted neighbouring carbon atom are shown in fig. 1 as a function of the partial hydrogen pressure over platinum black catalyst. The rates were calculated from the rate of appearance of the larger fragment of the molecule in the gas phase.

Fig. 2 illustrates the hydrogenolysis rates for the bonds between quaternary and primary C atoms per C—C bond (C_I—C_{IV}) calculated in a similar manner. In the case of 2,2,3,3-tetramethylbutane the gas phase contained 2,2,3-trimethylbutane in trace amounts only. Reactivity factors[9] are given in table 1, together with the literature data.

The *gem*-disubstituted pentanes have numerous other reaction possibilities: we observed dehydrogenation and isomerization as well as C_5- and C_6-cyclization. An example of the composition of the products is given in table 2. Fragmentation was the only reaction observed with neopentane and 2,2,3,3-tetramethylbutane under similar conditions (conversions 2.72 and 17.7%, respectively) whereas 2,2,3-trimethylbutane gave 4.93% fragments and 0.1% toluene.

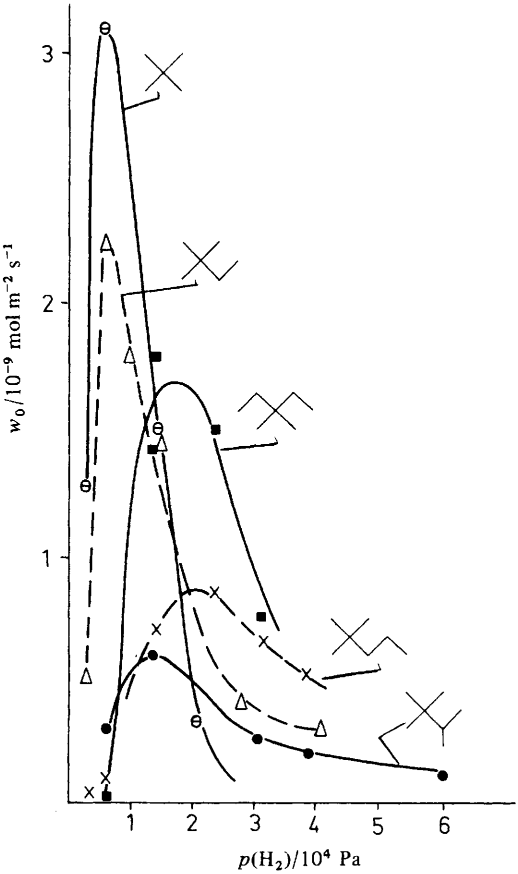
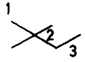
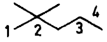
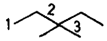
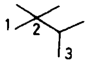
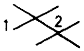


FIG. 2.—Initial rate of rupture of the C_I—C_{IV} bonds. Pt black catalyst, conditions as in fig. 1.

TABLE 1.—HYDROGENOLYSIS REACTIVITY FACTORS (ω) OVER Pt BLACK CATALYST, $T = 603$ K, $p(HC) = 1.23$ kPa, $p(H_2) = 2\text{-}60$ kPa

	$p(H_2)$/kPa	2.6	6.0	9.7	15.2	28.5	41.3	[a]
	ω_1 ω_2 ω_3	0.08 4.61 0.14	0.35 4.21 0.15	0.22 3.56 0.57	0.31 3.51 0.57	0.91 2.27 0.61	1.43 0.71 —	0.8 2.2 0.35
	$p(H_2)$/kPa	3.3	5.9	14.9	24.0	32.1	38.8	[a]
	ω_1 ω_2 ω_3 ω_4	0.09 5.22 — 0.50	0.14 5.10 — 0.47	0.51 4.13 — 0.33	0.57 3.90 — 0.39	0.49 3.72 — 0.82	0.46 3.67 — 0.95	0.25 3.7 0.09 1.45
	$p(H_2)$/kPa		6.3	14.5	24.2	31.3	39.5	
	ω_1 ω_2 ω_3		— 3 —	0.16 2.09 0.75	0.35 1.90 0.75	0.35 2.25 0.40	0.30 2.70 —	
	$p(H_2)$/kPa		6.4	14.1	31.1	39.1	61.3	[a]
	ω_1 ω_2 ω_3		0.01 5.95 0.01	0.02 5.92 0.01	0.03 5.88 0.01	0.08 5.72 0.02	0.20 5.17 0.12	0.7 2.7 0.6
								[a]
	ω_1 ω_2			< 0.01 > 6.94				0.45 4.3

[a] Ref. (9): $T = 573$ K, $p(HC) = 10$ kPa, $p(H_2) = 90$ kPa.

TABLE 2.—PRODUCT COMPOSITION (mol %) FROM 2,2- AND 3,3-DIMETHYLPENTANES. Pt BLACK CATALYST, $T = 603$ K, $p(\text{CH}) = 1.23$ kPa, $p(\text{H}_2) = 15$ kPa, AFTER 5 min CONTACT TIME.

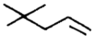
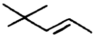
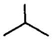
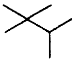
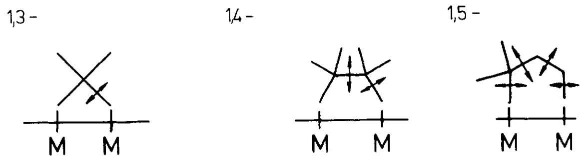
product	initial hydrocarbon 2,2-DMP	 3,3-DMP
$\Sigma < C_7$	1.49	2.63
	0.02	—
	0.08	—
	—	0.69
2,2-DMP	—	0.70
3,3-DMP	0.34	—
2-MHx	0.11	—
1,1-DMCP	6.82	2.82
toluene and/or DMCP$^{=}$	0.39	0.33
benzene	—	0.05
Σ conversion (%)	9.25	7.22

TABLE 3.—PRODUCT COMPOSITION (mol %) FROM ISOBUTANE, NEOPENTANE, 2,2,3-TRIMETHYLBUTANE AND 2,2,3,3-TETRAMETHYLBUTANE. 0.34 g Ni BLACK CATALYST, $T = 505$ K, $p(\text{HC}) = 1.23$ kPa, $p(\text{H}_2) = 4.3$ kPa, AFTER 5 min CONTACT TIME.

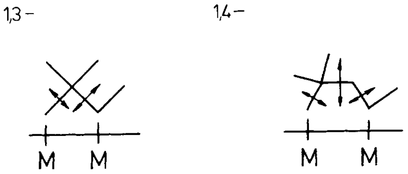
products	initial hydrocarbon 			
Σ conversion[a]	1.31	0.180	3.62	0.335
C_1	2.58	0.700	7.66	0.934
C_2	0.535	—	—	—
C_3	0.524	0.045	0.520	0.206
i-C_4	—	0.018	0.461	0.282
i-C_5	—	—	0.017	—
neopentane	—	—	1.60	—
neohexane	—	—	1.00	—
2,3-DMB	—	—	0.031	—

[a] Mol % of reactant consumed.

2,2,3,3-Tetramethylbutane was also reacted over nickel black catalyst. Similar bell-shaped curves (table 3) were observed for the formation of isobutane and propane. Some comparative experiments were also carried out with neopentane, 2,2,3-trimethylbutane and isobutane at constant hydrocarbon and hydrogen pressures. We observed maximum isobutane formation from 2,2,3,3-tetramethylbutane at this partial hydrogen pressure.



SCHEME 1.



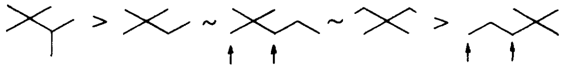
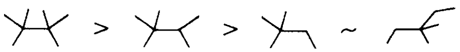
SCHEME 2.

DISCUSSION

PLATINUM BLACK CATALYST

We will first summarize our approach and expectations. Various diadsorbed species leading to C—C bond splitting can be presumed, *e.g.* terminal adsorption, scheme 1, and internal adsorption, scheme 2. 1,2-diadsorption is neglected owing to the higher activation barrier in ethane hydrogenolysis involving such adsorption.[13] Single or multiple metal–carbon bonds may be present.

If hydrogenolysis involved mainly or exclusively a particular type of adsorption, it would be possible to predict the sequence of reactivities of various hydrocarbons, on the basis of geometric and/or energetic considerations:

prevailing type of adsorption	expected reactivity order
internal 1,3-	
terminal 1,3-	
internal 1,4-	 > terminal 1,4-
terminal 1,4-	
terminal 1,5-	

We have found that (1) the bond between the quaternary carbon atom and its most substituted neighbour carbon atom is broken with the highest selectivity in all cases (table 1), (2) the order of reactivity for the rupture of this type of bond is (fig. 1): 2,2,3,3-TMB > 2,2,3-TMB > 2,2-DMB > 2,2-DMP ~ 3,3-DMP ~ neopentane, and (3) for the rupture of the C_I—C_{IV} bonds, a nearly opposite sequence was observed (fig. 2): neopentane > 2,2-DMB > 3,3-DMP > 2,2-DMP > 2,2,3-TMB ≫ 2,2,3,3-TMB.

Thus, the rate sequence for alkylsubstituted butanes supports the assumption of terminal 1,4-adsorption. The production of C_5-cyclic products from *gem*-dimethylpentanes (table 2) gives evidence also for the 1,5-interaction of the molecule with the catalyst. The slower demethylation can be explained by terminal 1,3-adsorption.

The hydrogenolysis rates measured at the maxima of the curves (fig. 1), where the hydrogen order becomes zero, increase as the C—C bond dissociation energy decreases in the different compounds. Such great differences were observed only between ethane and higher alkanes and were explained by the more favoured 1,3- and/or 1,2,3-adsorption of the latter species being responsible for the higher reactivity and lower energy of activation observed with larger molecules.[1, 13, 29] However, in hydrocarbons without quaternary carbon atoms at least one of the carbon atoms in the C—C bond to be broken may be attached to the surface and dissociated. The nearly random reactivity factors observed with platinum indicate that small differences like the different electric charges of the individual carbon atoms may be important in determining which carbon atom will be preferentially adsorbed.[11, 30, 31] Namely, terminal carbon atoms carry higher partial negative charges than secondary and especially tertiary carbon atoms.[31] On fresh catalysts, the initial adsorption of the latter types will be preferred, thus giving an enhanced probability of bond rupture to the internal positions [table 1 and ref. (9) and (11)]. According to Balandin's[32] concept of the energetics of catalytic reactions, their driving force must be hidden in the difference between the bonds to be broken and to be formed, including the bonds formed between the reactant and the catalyst. Assuming that the introductory phase of hydrogenolysis is C—H bond dissociation,[1] Balandin's equation should be for the breaking of a C—H bond over Pt (and forming H—Pt and alkyl—Pt species)

$$Q_{\mathrm{CH,\,Pt}} = Q_{\mathrm{C—H}} - Q_{\mathrm{H—Pt}} - Q_{\mathrm{C—Pt}}. \qquad (1)$$

Taking literature values for individual bond energies, with respect to primary, secondary and tertiary carbon atoms, the results are given in table 4, and show that energetics as expressed by eqn (1) must be an important factor in determining the direction of hydrogenolysis. This is true even if we do not consider the H—Pt and C—Pt bonds in eqn (1) to be chemically stable. The same conclusion can be drawn from spectroscopic data on mercury-alkyls where the experimentally determined force constants for the C—Hg bond were found to be 2.52 for ethyl, 2.37 for isopropyl and

TABLE 4.—ENERGIES INVOLVED IN THE INTERACTIONS OF VARIOUS CARBON ATOMS WITH Pt CATALYST

type of carbon atom	kJ mol^{-1}					
	$Q_{\mathrm{C—H}}$[a]	$Q_{\mathrm{H—Pt}}$[b]	$Q_{\mathrm{C—Pt}}$[c]	$Q_{\mathrm{CH,\,Pt}}$[c]	$Q_{\mathrm{C—Pt}}$[c]	$Q_{\mathrm{CH,\,Pt}}$[d]
primary	410	239	95	76	98	73
secondary	396	239	92	65	92	65
tertiary	381	239	89	53	86	57

[a] Ref. (28); [b] ref. (33); [c] the energy of the C_{II}—Pt bond has been taken from ref. (34), others were calculated assuming that the following ratio is valid: $Q_{\mathrm{Pt—C_I}}:Q_{\mathrm{Pt—C_{II}}}:Q_{\mathrm{Pt—C_{III}}} = Q_{\mathrm{H—C_I}}:Q_{\mathrm{H—C_{II}}}:Q_{\mathrm{H—C_{III}}}$; [d] as in note (*c*) but using the force constant ratios of Hg-alkyls from ref. (35): $Q_{\mathrm{Pt—C_I}}:Q_{\mathrm{Pt—C_{II}}}:Q_{\mathrm{Pt—C_{III}}} = Q_{\mathrm{Hg—C_I}}:Q_{\mathrm{Hg—C_{II}}}:Q_{\mathrm{Hg—C_{III}}}$.

TABLE 5.—C—C BOND DISSOCIATION ENERGY AND RELATIVE REACTIVITIES OF SOME HYDROCARBONS

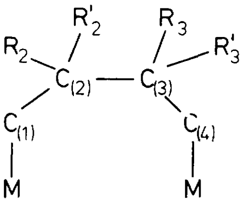
C—C energy[a] /kJ mol^{-1}	alkyl groups	corresponding substituents in scheme 3				alkane	relative reactivity of the C_2—C_3 bond rupture[b]
		R_2	R_2'	R_3	R_3'		
343	ethyl-ethyl	H	H	H	H	n-butane	not measured
335	ethyl-isopropyl	CH_3	H	H	H	2-methylbutane	not measured
322	ethyl-t-butyl	CH_3	CH_3	H	H	2,2-dimethylbutane	1.00
306	isopropyl-t-butyl	CH_3	CH_3	CH_3	H	2,2,3-trimethylbutane	2.82
283	t-butyl-t-butyl	CH_3	CH_3	CH_3	CH_3	2,2,3,3-tetramethylbutane	4.06

[a] Ref. (28). [b] Measured at the maxima of the reaction rate against $p(H_2)$ curves, conditions given in fig. 1.

2.22 for t-butyl substituents (in N cm^{-1}).[35] $Q_{CH, Pt}$ values for different types of carbon atoms calculated from Hg-alkyls are in fair agreement with data extrapolated from C—H bond energy values (table 4).

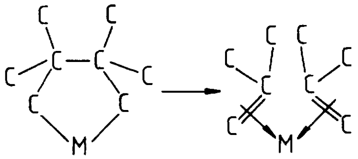
Another factor influencing the energetics of bond rupture is the possibility of π-allylic interaction whenever 1,2,3-adsorption is possible. This means a considerable lowering of the energy of activation calculated on the basis of Balandin's equations.[36]

The situation is totally different with 1,4-adsorption. Here the C—M bonds are not formed with the participation of the carbon atom of the C—C bond to be broken and, owing to the quaternary character of at least one of the carbon atoms, π-allylic interactions are not possible. Here the energy of the C—C bond to be cleaved will influence the reaction more directly. The situation is shown in scheme 3 and the corresponding data are shown in table 5. The relative reactivities of substituted butanes with quaternary carbon atoms are inversely proportional to the C_2—C_3 bond energy. No measurements are shown for n-butane and methylbutane, where 1,2,3,-adsorption may overcompensate the effect of changing bond energy.



SCHEME 3.

As distinct from this Anderson-type reaction involving at least two metal atoms, another possibility would be the formation of metalacyclopentane with participation of one metal atom (scheme 4). Analogous metalacyclobutanes were proposed by O'Donohoe *et al.*[37] Such organometallic complexes are known to form surface π-complexes, as shown in scheme 4.†



SCHEME 4.

The position of the maxima in the hydrogenolysis curves is shifted towards higher partial hydrogen pressure with increasing carbon number. This is in agreement with the results of Gault and coworkers[22] who found the same tendency for hydrocarbons containing no quaternary C atom. We agree with Leclercq *et al.*[19] who believe that it is due to the adsorption properties of the hydrocarbons. With increasing carbon number, the 'coefficient' for the reactive adsorption of the hydrocarbons increases and the molecule can more easily displace hydrogen on the reactive sites. It would be desirable to check this hypothesis by more direct measurements of hydrocarbon and hydrogen coadsorption.

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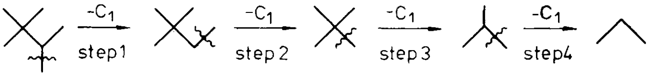
† We thank one of the referees for drawing our attention to this point.

The 'lazy' C—C splitting of the *gem*-dimethylpentanes indicates that their internal 1,4-type adsorption either is not predominant or does not occur at all. The behaviour of 3,3-dimethylpentane gives us a further information: though the structure of the molecule would permit a terminal 1,4-interaction with the metal surface, it does not play an important role compared with 1,5-type adsorption (*cf.* table 2). This strong tendency for terminal adsorption can be interpreted either by assuming a dicarbyne-type surface species in hydrogenolysis,[38] or by simple steric effects; that is, the end methyl groups of a long carbon chain are the most accessible for the catalyst surface atoms. Formation of metalacyclohexanes (analogously to scheme 4) should be sterically preferential. This species should, however, lead to another type of C—C bond splitting analogous to the 'ring opening' of cyclopentanes.[3]

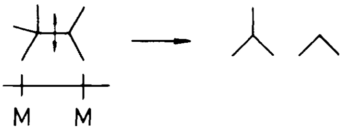
NICKEL BLACK CATALYST

Nickel selectively cleaves terminal C—C bonds.[3, 6, 13] Due to the strong interaction between nickel and hydrocarbon, hydrogenolysis is confined to the place of primary adsorption and presumably involves 1,2-interaction.[29] Such adsorption is impossible with neopentane and 2,2,3,3-tetramethylbutane and these molecules undergo fragmentation at a rate which is almost an order of magnitude slower (table 3). Tetramethylbutane also gives isobutane and propane as well as methane. Their appearance (and the lack of detectable amounts of larger demethylated fragments, *i.e.* 2,2,3-trimethylbutane, neohexane and neopentane) serves as evidence of direct internal C—C bond rupture over nickel.

The example of 2,2,3-trimethylbutane shows that the C—C bond rupture commences where 1,2-interactions are possible, giving considerable amounts of neohexane and neopentane. Isobutane and propane formation can also be explained by the same consecutive mechanism (scheme 5). There is also another possibility for the cleavage of the central bond: direct rupture caused by a 1,4-type interaction with the metal (scheme 6). With tetramethylbutane only scheme 6 may be operative. The comparison cf C_4 and C_3 fragment yields from trimethyl- and tetramethyl-butanes indicates that their formation *via* direct and stepwise fragmentation (schemes 5 and 6, respectively) should occur with comparable rates.



SCHEME 5.



SCHEME 6.

To select between possible pathways, we calculated the ratio of fragments of two consecutive demethylating steps

$$\frac{[C_{i-1}H_{2(i-1)+2}]}{[C_iH_{2i+2}]}$$

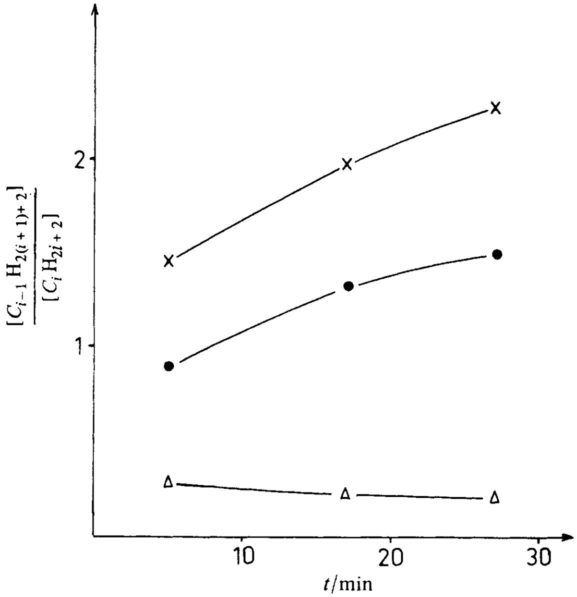


FIG. 3.—Ratios of concentration of the $(i-1)$th fragment to the concentration of the ith fragment from 2,2,3-trimethylbutane as a function of reaction time. Ni black catalyst, conditions as in table 3. ×, neopentane/neohexane; ●, propane/isobutane; △, isobutane/neopentane.

as a function of the reaction time (fig. 3). In the case of an exclusive consecutive mechanism, we would expect all these values to increase with increasing contact times. Instead we found decreasing isobutane/neopentane ratios (step 3) while the neopentane/neohexane (step 2) and propane/isobutane (step 4) conversion ratios increased. This clearly indicates that for isobutane formation there is another pathway. The relatively low isobutane/neopentane ratio means that this other reaction route is not favoured. The propane/isobutane ratio is, at the beginning, near to unity, as expected from scheme 6, and the difference in favour of isobutane indicates the occurrence of scheme 5.

The methane balance also gives evidence for the direct rupture of internal C—C bonds. If all the smaller hydrocarbon products were formed by consecutive demethylation according to scheme 5, the methane balance should be written as

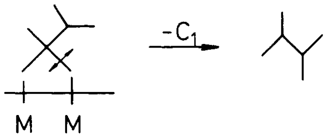
$$[C_1] = [\text{neohexane}] + 2[\text{neopentane}] + 3[\text{isobutane}] + 4[\text{propane}] + 5[\text{ethane}] \quad (2)$$

for 2,2,3-trimethylbutane. These calculated $[C_1]$ values are compared with the experimental data in table 6. In the case of isobutane and neopentane, methane formation is always greater than the calculated values, which means that there is also extensive breakdown of ethane (scheme 5). On the contrary, 2,2,3,3-tetramethylbutane gives much less methane than the calculated amount, which indicates direct C_{IV}—C_{IV} bond cleavage (scheme 6). 2,2,3-Trimethylbutane represents an intermediate type: the calculated methane yield is greater than the experimental yield at the beginning of the reaction but with increasing contact time extensive demethylation should prevail.

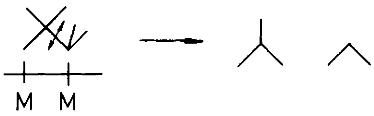
The above points indicate that several types of adsorption can occur simultaneously: mainly 1,2-adsorption leading to demethylation and 1,4-adsorption resulting in rupture of the central bond. Demethylation can also occur through 1,3-adsorption,

TABLE 6.—METHANE BALANCE FOR SOME HYDROCARBONS AS A FUNCTION OF REACTION TIME. Ni BLACK CATALYST, CONDITIONS GIVEN IN TABLE 3.

hydrocarbon	time /min	calc. $[C_1]$ (mol %)	measured $[C_1]$ (mol %)
isobutane	5	1.6	2.6
	12	6.6	15
	21	12	32
	31	20	54
neopentane	5	0.11	0.70
	15	0.24	1.94
	25	0.36	2.62
	35	0.41	3.2
2,2,3-trimethylbutane	5	6.6	6.1
	17	25.0	37.0
	27	41.0	70.0
2,2,3,3-tetramethylbutane	2	0.77	0.27
	4.5	1.94	0.84
	7	3.1	1.5
	9.5	4.0	2.3
	18	8.5	5.8
	23.5	11.4	8.7



SCHEME 7.



SCHEME 8.

as in the case of neopentane, but this reaction is much slower (scheme 7). This reaction may have given 2,3-dimethylbutane and isopentane from 2,2,3-trimethylbutane (table 3). We cannot exclude an internal 1,3-type interaction of 2,2,3-trimethylbutane (scheme 8), although the contact of the tertiary carbon atom with the surface is sterically hindered. Regarding the relative inactivity of 1,3-type interactions (see table 3), we think that internal C—C bond rupture *via* 1,4-interactions may be more favoured.

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