JOURNAL OF CATALYSIS **93**, 399–408 (1985)

The Hydrogenolysis of Alkanes on $Mo(0)/Al_2O_3$ Catalysts

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Received September 21, 1984; revised December 14, 1984

The hydrogenolyses in a pulse reactor of propane, butane, isobutane, pentane, isopentane, cyclopentane, and neohexane occur at roughly equal rates on $Mo(0)/Al_2O_3$, but those of ethane and neopentane are slower and that of cyclopropane is several times faster. With large enough alkanes, single hydrogenolysis was accompanied by double and triple hydrogenolysis as initial reactions, but the C_2(ads) fragment underwent further cleavage rather slowly. Cleavage of both terminal and medial bonds was observed, but that of terminal bonds predominated. The activity of $Mo(0)/Al_2O_3$ is roughly equal to that of Ir/Al_2O_3, but divergence among the rates of hydrogenolysis of various alkanes is smaller on $Mo(0)/Al_2O_3$. Since butenes gave rates of hydrogenolysis at 300°C about equal to that of butane, a 1,2-diadsorbed alkane is not likely to be an intermediate in hydrogenolysis. The rate of hydrogenolysis of propane and butane and the degree of multiple hydrogenolysis of cyclopropane increased rapidly as the average ON (oxidation number) of the molybdenum decreased in the series, $ON \cong +4$, $ON \cong +2$, and $ON = 0$, but the rate of hydrogenolysis of cyclopropane changed little. The hydrogenolysis of alkanes is likely to involve two or more simultaneous mechanisms occurring at significant rates.

INTRODUCTION

The preceding paper (*1*) reports that propane is hydrogenolyzed on several $Mo(0)/Al_2O_3$ catalysts and that clean metallic molybdenum on dehydroxylated alumina, Mo(0)/DA, is much more active for this reaction than Mo/Al_2O_3 catalysts in which the oxidation number of Mo is greater than zero. This paper reports a study of the hydrogenolysis of a number of other alkanes on Mo(0)/DA prepared in most cases by treating $Mo(CO)_6$/DA by He,500°,1;He,650°,0.1;H_2,650–950°,1 (where He,500°,1 means that the catalyst was heated in flowing helium for 1 hr at 500°C). A pulse reactor was employed in these studies.

EXPERIMENTAL

Propane, butane, isobutane, and ethylene were from Matheson, 99.5% min. purity. Butenes were from Phillips Petroleum Company, 99% min. purity. Pentane was Mallinckrodt Nanograde and 2-methylbutane, hexane, neohexane, and cyclopentane were from Chemical Samples Company, 99.9%. All samples were purified in the apparatus by several bulb-to-bulb distillations designed to eliminate oxygen. The hydrocarbon vapor could then be admitted to the 1.0-cm^3 loop of the injection valve. The size of the injected pulse was controlled by adjusting the pressure in the loop as measured by a capacitance manometer with digital output. Usually either 12.4- or 25.1-μmol pulses of hydrocarbon were employed. Hydrogen (Matheson, UHP) used during hydrogenolysis runs was passed through a Deoxo unit and then through a trap of silica gel (Davison Grade 62) at −196°C to remove any gases boiling above hydrogen. Flow rates of hydrogen were chosen so as to keep conversions low. A trap of Mn^{2+}/SiO_2 located between the injection valve and the catalyst removed any adventitious oxygen. A trap of silica gel at −196°C followed the reactor. Products and unconverted reactant were collected here. Warming the trap released products and re-

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0021-9517/85 $3.00

TABLE 1

Hydrogenolysis of Butane in Pulse Experiments[a]

Catalyst[b]	Pretreatment[c]	250°C		300°C	
		N_t[d] (sec^{-1})	C_1/C_3[e]	N_t[d] (sec^{-1})	C_1/C_3[e]
P1, 3.5 μmol/PDA	H_2,450°,1			0.005	~1
	H_2,650°,1[f]			0.025	3.3
	H_2,800°,1[f]			0.21	9.3
	H_2,950°,1[f]			0.19	8.9
P2, 3.0 μmol/DA	H_2,650°,1	0.072	3.8	0.25	4.5
P3, 4.2 μmol/DA	H_2,650°,1			0.21	5.0
	H_2,960°,1[f]			0.18	4.9
	H_2,950°,1[f]			0.20	4.9
P4, 3.8 μmol/DA	H_2,650°,0.5	0.073	3.7		
P5, 3.2 μmol/DA	H_2,650°,0.5	0.078	3.7		
P6, 1.7 μmol/DA	H_2,650°,0.5			0.18	2.5
P7, 3.8 μmol/DA	H_2,650°,1	0.058	5.2		

[a] A 25.1-μmol pulse of butane was used for catalysts P1–P5. For catalysts P6 and P7 12.4-μmol pulses were employed. The numbers refer to the results with an early pulse, usually about the second pulse. Since the maximum conversion in any listed experiment was 14% (8% at 250°C), values of C_1/C_3 should not be seriously distorted by secondary hydrogenolysis.

[b] The number of μmol of $Mo(CO)_6$ on 0.05 g of alumina.

[c] Catalyst P1 was first treated He,500→450°. The other catalysts were first treated He,500°,1;He,650°,0.1.

[d] Turnover frequency per atom of Mo for the hydrogenolysis of butane at the listed temperature.

[e] The ratio (moles CH_4)/(moles C_3H_8) in the product.

[f] The preceding catalyst was given the listed treatment.

actants as a sharp pulse into flowing hydrogen for gas chromatographic separation and measurement. The general experimental procedures and also the procedures for preparing and activating the $Mo(CO)_6/Al_2O_3$ catalysts have been described (*1*, *2*).

EXPERIMENTAL RESULTS

Pulse Behavior

The injection valve was a jacketed Carle microvolume valve. Helium was circulated through the jacketed region to eliminate leakage of oxygen into the carrier gas stream. The output of the valve was connected in one case as directly as possible to the catharometer so as to permit the estimation of the pulse width at the entrance to the catalyst bed. At a hydrogen flow rate of 150 cm^3 min^{-1} the pulse widths of both 12.4- and 25.1-μmol pulses of butane (0.3 and 0.6 atm, respectively) were about 8 sec.

A series of 25.1-μmol butane pulses was passed over catalyst P4 (Table 1) at 250°C at various values of the hydrogen flow rate, L. The conversion per pulse was proportional to $1/L$ between 70.5 and 300 cm^3 min^{-1} (22.0–4.9% hydrogenolysis of butane). At 37.5 cm^3 min^{-1}, the conversion was somewhat low, 37% vs a predicted 40%. It follows that the pulse width was inversely proportional to L over the range of L used in this work.

The effect of varying the pulse size at a constant flow rate of 300 cm^3 min^{-1} was investigated at 250°C. Results are shown in Table 2. The increase in yield with increasing pulse size probably results from the rate being proportional to some fractional power of the pressure of butane.

TABLE 2

Effect of Pulse Size upon Conversion of Butane on Catalyst P5 at 250°C, Flow Rate of H_2 = 300 cm^3 min^{-1}

Pulse size, μmol	1.2	4.78	12.4	25.1	36.0
Yield relative to 12.4 μmol	0.33	0.55	(1.00)[a]	1.45	1.52

[a] Pulses of 12.4 μmol were scattered among the pulses of other sizes. The yields in the 12.4-μmol pulses decreased from 0.69 to 0.64 μmol during the sequence. The appropriate value of the yield for 12.4 μmol was chosen for each of the other pulse sizes in order to calculate the relative yield.

Calculation of N_t. The kinetic form of hydrogenolysis on various Mo/Al_2O_3 has not been studied, but a few isolated experiments suggest that the rate is proportional to some fractional power of the pressure of alkane. Thus, N_t's cannot be calculated accurately from pulse experiments. However, we present some values of N_t calculated assuming that the pulse width is 8(150/L) sec and choosing a 25.1-μmol pulse since the average pressure of alkane in such a pulse at the catalyst would be about 0.03 atm given the original pressure in the loop. This is close to the pressure employed in the flow experiments (*1*). Thus, for example a 12.4-μmol pulse of propane in hydrogen flowing at 300 cm^3 min^{-1} and passed over catalyst P7 at 250°C lost 0.63 μmol of propane. Whence,

$$N_t = \frac{1.45 \times 0.63}{3.8 \times 4} = 0.060 \text{ sec}^{-1},$$

where 1.45 converts the yield from 12.4 to 25.1 μmol, 3.8 is micromoles of Mo and 4 is the pulse width at L = 300 cm^3 min^{-1}. In the flow reactor, N_t was 0.06 (Table 5 of Ref. (*1*)). Such agreement is clearly fortuitous.

RESULTS OF HYDROGENOLYSES

In general, butane was used as the reference compound in the work of this paper. The hydrogenolyses of a number of hydrocarbons were examined on catalyst P7 at 250°C. In all cases, 12.4-μmol pulses were employed and L was 300 cm^3 min^{-1}. Pulses of butane were dispersed through those of the other hydrocarbons. The reactivities of the various hydrocarbons relative to butane are given in Table 3. On catalyst P4 at 250°C the relative activity for hydrogenolysis of ethane was 0.18 and that of ethylene was 0.28.

After catalyst P2 had been regenerated by H_2,650°,0.5 to about 85% of its initial activity for the hydrogenolysis of butane, 36.4-μmol pulses of butenes were passed over the catalyst at 250°C in hydrogen flowing at 300 cm^3 min^{-1}. 1-, *cis*-2-, and *trans*-2-butene all gave about the same yield of hydrogenolytic products, 0.95 μmol methane, 0.62 μmol ethane, and 0.33 μmol propane as well as 13.0 μmol butane. (The remaining material was a mixture of butenes, isomerized only part way to equilibrium.) Butane gave about the same yield of hydrogenolysis products as the butenes.

The relative rates of the hydrogenolysis of normal alkanes were investigated at 300°C, 12.4-μmol pulses, H_2 at 150 cm^3 min^{-1} on catalyst P6. N_t's for propane, bu-

TABLE 3

Activity for Hydrogenolysis of Various Hydrocarbons Relative to Butane on Catalyst P7 at 250°C

Hydrocarbon	Relative activity	N_t[b] (sec^{-1})
Ethane	0.09	0.007
Ethylene	0.12[a]	0.009
Propane	0.8	(0.06)
Cyclopropane	5.1	0.38
Butane	(1.00)	0.08
Isobutane	1.0	0.08
Pentane	1.4	0.10
Isopentane	1.5	0.11
Neopentane	0.25	0.02
Cyclopentane	0.9	0.07
Neohexane	0.8	0.06

[a] The remaining ethylene was entirely converted to ethane.

[b] Calculated from N_t for propane in a flow reactor (Table 5 of Ref. (*1*)) and the relative activities.

TABLE 4

Hydrogenolysis of Various Alkanes on Catalyst P7 at 250°C; 12.4-μmol Pulse; Flow Rate of H_2 300 cm^3 min^{-1}

	Products (μmol)											
Pulse No.	3	4	5	6	8	10	11	12	13	14	15	
Alkane[a]	n-C_4	i-C_4	C_3	neo-C_5	neo-C_6	n-C_5	i-C_5	n-C_4	c-C_5[b]	c-C_3[c]	n-C_4	c-C_5[d]
-Δ(Alkane)[e]	0.88	0.87	0.63	0.20	0.62	1.08	1.13	0.75	0.65	3.81	0.75	0.60
CH_4[f]	1.36	1.25	0.85	0.48	0.97	1.53	1.71	1.16	1.21	3.10	1.15	1.07
C_2H_6	0.69	0.35	0.52	0.075	0.48	0.76	0.59	0.59	0.33	1.63	0.58	0.16
C_3H_8	0.26	0.51	—	0.093	0.15	0.57	0.43	0.23	0.26	1.66	0.23	0.12
n-C_4H_{10}	—	0.00		0.00	~0.04	0.16	0.20	—	0.13			0.09
i-C_4H_{10}	0.00	—		0.025	0.24	0.00	0.17	0.00	0.00			0.00
c-C_5H_{10}[b]				0.00	0.00	0.00	0.00		—			—
n-C_5H_{12}				0.00	0.00	—	0.00		0.01			0.18
i-C_5H_{12}				0.00	0.03	0.00	—		0.00			
neo-C_5H_{12}				—	~0.005	0.00	0.00		0.00			

[a] The alkane injected.

[b] Cyclopentane.

[c] Cyclopropane.

[d] On partially deactivated catalyst P2.

[e] Total moles of alkane reactant converted into hydrogenolyzed products.

[f] μmol methane in the product. C_2H_6 and other entries below this are also products.

tane, pentane, and hexane were all 0.18–0.20, but that for ethane was 0.07.

Although the matter was not investigated in detail, it appears likely that relative rates of hydrogenolysis of various hydrocarbons varied with the degree of catalyst deactivation. Thus, on catalyst P2 at 250°C at a level of deactivation of nearly 50%, cyclopentane reacted 1.8 times as fast as butane in the runs before and after cyclopentane, but on catalyst P7 (Table 4), butane reacted slightly faster. Further, as shown in Table 4, the relative yield of pentane from the hydrogenolysis of cyclopentane was much larger than with catalyst P7. Following cyclopentane, the rates of hydrogenolysis relative to butane were neopentane 0.36, cyclohexane, 1.65, and neohexane 1.6. Cyclohexane gave a small yield of benzene.

In general, products of single, double, triple, etc. hydrogenolyses were observed in initial products as shown in Table 4. All conversions here were less than 9% so that little contribution from subsequent hydrogenolysis of products of the initial hydrogenolysis should have occurred. In other experiments at high conversions, the proportion of methane rose and at severe enough conditions, the product was entirely methane (*1*).

Catalyst preparations were rather reproducible. Catalysts P2, P3, P4, and P5 gave data in good agreement. N_t(250°C) for P7 corrected to 25.1 from 12.1 μmol by the data of Table 2 would be 0.84 sec^{-1}, a little higher than the N_t's of P2–P5 and C_1/C_3 was also high. Corrected to 25.1 μmol, N_t for P6 was high but C_1/C_3 was low. However, the loading of P6 by Mo was only one-half that of the other catalysts.

In general, both catalyst activity and C_1/C_3 decreased slowly with pulse number, but regeneration by H_2,950° restored both to the initial values. However, a subsequent H_2,950°,1 reduced the anomalously high value of C_1/C_3 of Catalyst P_1 after its first exposure to H_2,950° to a normal value.

In general, C_1/C_3 increased with increasing temperature. This is illustrated for catalyst P2 in Table 5.

TABLE 5

Values of N_t and C_1/C_3 for Butane on Catalyst P2

Temp. (°C)	N_t	C_1/C_3	N_t(flow)[a]
200	0.0092	3.0	0.0046
250	0.072	3.8	0.060
300	0.25	4.5	0.55

[a] Values of N_t for *propane* in the flow reactor from Table 5 of Ref. (*1*).

In a few cases, at lower temperature on deactivated catalysts, only single hydrogenolysis was observed. For example, on a deactivated catalyst at 185°C, the conversion of hexane was 0.03%. The yields of methane, ethane, propane, butane, and pentane were nearly equal. Here, then, it appeared that all bond cleavages were equally likely. Pentane on a deactivated catalyst at 200°C at a similar low conversion gave $CH_4 = C_4H_{10} = 0.5(C_3H_8) = 0.5(C_2H_6)$. Thus, here, cleavage of the inner bonds of pentane was about twice as probable as the outer ones. In hydrogenolysis of butane on catalyst P3, poisoned by O_2 and partially regenerated (Fig. 2 of Ref. (*1*)), C_1/C_3 was low, 3.2 at 300°C after H_2,650° vs 4.9 after H_2,950°.

Hydrogenolysis of cyclopropane. Data on the hydrogenolysis of cyclopropane at 250–300°C appear in Table 6 for the following reactions

$$\text{c-}C_3H_6 + H_2 \rightarrow C_3H_8 \qquad (1)$$

$$\text{c-}C_3H_6 + 2H_2 \rightarrow C_2H_6 + CH_4 \qquad (2)$$

$$\text{c-}C_3H_6 + 3H_2 \rightarrow 3CH_4 \qquad (3)$$

After catalyst P1 had been regenerated by H_2,950°,0.5 to near normal activity a 5.2-μmol pulse of cyclopropane was passed over the catalyst in helium carrier at 300°C. One half was converted to propylene, $N_t \simeq 0.04\ \text{sec}^{-1}$.

DISCUSSION

General Characteristics of Hydrogenolysis

The hydrogenolysis of butane on Mo(0)/DA closely resembled that of propane. As shown in Table 1, rates at 250°C were close to those of propane (Table 5 of Ref. (*1*)) although the ratio $N_t(300°)/N_t(250°)$ was smaller than in the flow reactor with propane (Table 5). The rather large ratio of yields, methane/propane (~5 at 300°C), shows that substantial multiple hydrogenolysis occurred as an initial reaction. The value of the ratio would be unity if there

TABLE 6

Hydrogenolysis of Cyclopropane

Catalyst	T (°C)	Pulse size (μmol)	N_t (sec^{-1})	$N_t(1)$[a] (sec^{-1})	$N_t(2)$[a] (sec^{-1})	$N_t(3)$[a] (sec^{-1})	N_t(isom)[b] (sec^{-1})
P7[c]	250	12.4	0.25	0.11	0.11	0.03	0.000
P1[d]	300	25.1	0.53	0.51	0.02	—	0.15
P1[e]	300	25.1	0.97	0.91	0.05	0.005	0.02
P1[f]	300	25.1	0.69	0.35	0.25	0.086	0.000
P3[g]	300	25.1	0.18	0.133	0.046	0.000	0.000

[a] Turnover frequencies for single ($N_t(1)$), double ($N_t(2)$), and triple ($N_t(3)$) hydrogenolyses per atom of Mo.

[b] Turnover frequency per Mo for isomerization to propylene.

[c] Pulse 14 of Table 4.

[d] Value for six successive pulses of cyclopropane after initial activation, H_2,450°,1 (see Table 1). There were other products than propane and propylene in low yield, probably products of metathesis.

[e] After subsequent H_2,650°,1.

[f] After subsequent H_2,800°,1;H_2,950°,1.

[g] After poisoning by CO (see Ref. (*1*)). N_t for the hydrogenolysis of propane was reduced to 0.008 sec^{-1}.

was no multiple hydrogenolysis. Whether the final exposure to hydrogen during pretreatment was at 650 or at 950°C had little effect upon N_t or C_1/C_3 (catalyst P3 in Table 1).

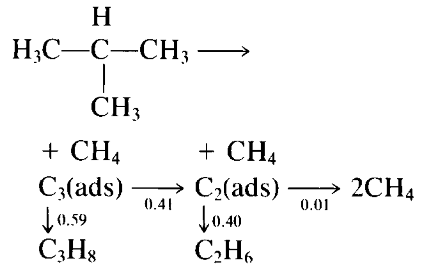
In $Mo(CO)_6$/PDA;He,600°, the average ON is ~5.6 (*2*). As this material was exposed to hydrogen at successively higher temperatures, the activity levels for hydrogenolysis rose from slight after 450°C to modest at 650°C. After 800 and 950°C, under which conditions metallic Mo on alumina had been formed (*1*), N_t was the same as on Mo(0)/DA catalysts prepared by $Mo(CO)_6$/DA;He,500°;H_2,650°. As with propane (*1*), the degree of multiple hydrogenolysis steadily increased as the temperature of pretreatment in H_2 rose from 450 to 800°C.

No formation of isomers of the alkane fed was observed with butane or the other alkanes investigated including neopentane and neohexane. It appears that the rate of isomerization did not exceed 0.02 that of hydrogenolysis. Further, formation of $C_{n+1}H_{2(n+1)+2}$ from C_nH_{2n+2} was not observed.

Results of Hydrogenolysis of Various Alkanes

Table 3 shows relative conversions and rough values of N_t per atom of Mo in the hydrogenolysis of several alkanes at 250°C on the somewhat anomalous catalyst P7 (high C_1/C_3 for butane) using 12.4-μmol pulses of alkanes. The vapor pressures of alkanes of higher boiling points than these were too low at 25°C to permit injection of 12.5-μmol pulses of such alkanes. As reported under Experimental, relative rates of hydrogenolysis may vary with catalyst deactivation, with the temperature of the hydrogenolysis run and among catalyst preparations. However, it appears safe to conclude that the rates of the alkanes studied were within a factor of 2 except for cyclopropane which was faster and for ethane and neopentane which undergo hydrogenolysis slower than the other alkanes.

Propane shows simultaneous, initial, single hydrogenolysis to $C_2H_6 + CH_4$ and double hydrogenolysis to $3CH_4$ (Table 4). One might assume that the two processes occur on separate types of sites, but results with hexane make such an idea appear unattractive. Here the products are pentane, butane, propane, and ethane as well as methane and the assumption that there are four different kinds of sites would appear rather forced. It seems more likely that adsorbed alkanes undergo cleavage into two fragments which can either react with H* to release alkanes or which can undergo further fragmentation (except for C_1 fragments). On this basis, the hydrogenolysis of isobutane in Table 4 can be represented



$$\mathrm{H_3C{-}\overset{H}{\underset{CH_3}{C}}{-}CH_3} \longrightarrow$$

$$\begin{tikzcd} \overset{+\,\mathrm{CH_4}}{\mathrm{C_3(ads)}} \arrow[r, "0.41"'] \arrow[d, "0.59"] & \overset{+\,\mathrm{CH_4}}{\mathrm{C_2(ads)}} \arrow[r, "0.01"'] \arrow[d, "0.40"] & \mathrm{2CH_4} \\ \mathrm{C_3H_8} & \mathrm{C_2H_6} & \end{tikzcd}$$

such that hydrogenolysis of isobutane occurs 59% to $C_3H_8 + CH_4$, 40% to $C_2H_6 + 2CH_4$, and 1% to $4CH_4$. Here cleavage of C_2(ads) is slow and zero to within the experimental error. Hydrogenolysis of neopentane can be similarly represented as 12.4% to i-$C_4H_{10} + CH_4$, 46.1% to $C_3H_8 + 2CH_4$, 37.2% to $C_2H_6 + 3CH_4$, and 4.4% to $5CH_4$. Triple hydrogenolysis occurs to a substantial extent in forming the initial products and again cleavage of C_2(ads) is slow. However, cleavage of C_2(ads) in the hydrogenolysis of propane is relatively faster since propane forms 83% $C_2H_6 + CH_4$ and 17% $3CH_4$ (Table 4).

This type of calculation cannot be extended to butane or any pentane except neopentane. With butane, for example, initial cleavage might occur either to form C_1(ads) + C_3(ads) or to form $2C_2$(ads). There is one more variable than data and a single solution is impossible. Thus, for pentane,
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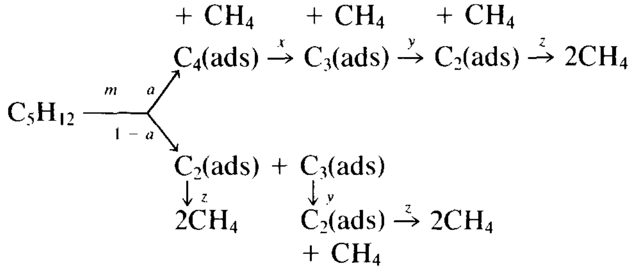


where m is the moles of pentane reacting, a is the fraction which undergoes initial cleavage at the terminal bond and $1 - a$ undergoes cleavage at a medial bond, x is the fraction of C_4(ads) which undergoes further cleavage to C_3(ads) + CH_4 and $1 - x$ is the fraction which forms C_4H_{10}, etc. There are four extensive variables but only three intensive variables, the mole fractions of C_4H_{10}, C_3H_8, and C_2H_6 (the fraction of CH_4 is not an intensive variable).

If a is assumed to be unity (no medial cleavage), one can calculate that the amount of CH_4 which must be made to give the observed yields of C_2H_6, C_3H_8, and C_4H_{10} would be 3.58 μmol, over twice the 1.53 μmol of CH_4 observed. The excess of CH_4 similarly calculated from Table 4 for butane is much smaller. However, on catalyst P2 at 250°C, butane gave less multiple hydrogenolysis and the yields were C_3H_6, 0.61 μmol; C_2H_6, 1.33 μmol; and CH_4, 2.34 μmol. The yield of CH_4 calculated assuming that $1 - a$ was zero is 3.27 μmol, distinctly above the observed value.

As noted above, z is very small for cleavage of C_2(ads) during the hydrogenolyses of isobutane and neopentane. If we assume that z is zero for pentane, one variable is eliminated and a solution becomes possible: $a = 0.620$, $x = 0.761$, and $y = 0.380$. This calculation cannot be exact but it seems safe to conclude that on catalyst P7 both terminal and medial cleavage occur initially and that terminal cleavage predominates.

Of course, the sites on the surface of the molybdenum particles are apt to be nonuniform and the values of a, x, etc. calculated above are averages which may well vary from catalyst to catalyst (see cyclopentane in Table 4). Presumably, more experience with Mo(0)/DA will lead to better reproducibility in catalyst preparation.

Neohexane must also undergo substantial medial cleavage (at the isobutyl–ethyl bond). In the run in Table 4, the calculated yield of methane assuming that all initial cleavages are at a terminal bond is 2.93 μmol whereas only 0.97 μmol was observed.

Comparison of Mo/Al$_2$O$_3$ with Other Hydrogenolysis Catalysts

It is impossible to give a single ordering of turnover frequencies per M_s for the hydrogenolysis of alkanes on various metals since the ratio of N_t's per M_s for a particular pair of metals appears to vary with metal particle size and other characteristics of the supported metal catalysts, with the alkane hydrogenolyzed, with temperature, and with P_{H_2} (*3–6*). However, for many particular combinations of alkane, temperature, and P_{H_2}, ruthenium is the most active catalyst, with rhodium, iridium, or osmium next (*6*). It is not easy to select from the literature (*7–9*) a value of N_t for the ruthenium-catalyzed hydrogenolysis of even only propane or butane. For one reason, the contribution of Cl^- in metal/Al$_2$O$_3$ catalysts is not clear. However, it appears that ruthenium is at least an order of magnitude faster per M_s than molybdenum (or molybdenum carbide) on alumina.

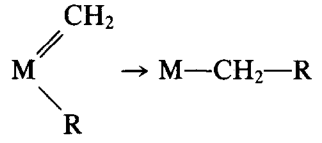
Anderson and Foger (*10*) examined the hydrogenolysis of ethane, butane, isobutane, neopentane, and neohexane on a catalyst prepared from $Ir_4(CO)_{12}/Al_2O_3$ under conditions close to those of propane on Mo/Al_2O_3 in a flow reactor (*1*). Differences among the values of N_t for these alkanes were much larger on Ir/Al_2O_3 than on Mo/Al_2O_3. From the data of Ref. (*10*) and of Table 3 of the present paper with the assumption that the percentage exposed of Mo is 30%, at 250°C N_t per M_s for butane on Ir/Al_2O_3 is 7 times larger than that on catalyst P7, N_t for neohexane is 1.7 times larger, N_t for neopentane and ethane are 0.14 times larger, and N_t for isobutane is 0.04 times larger. Thus, Mo/Al_2O_3 and Ir/Al_2O_3 have roughly equivalent hydrogenolytic activities per M_s and Mo/Al_2O_3 ranks among the more active hydrogenolysis catalysts. This rather high activity makes it questionable as to whether one can correlate hydrogenolytic activity monotonically with mere percentage *d*-band character of the metal.

The classification of hydrogenolysis catalysts proposed by Paál and Tétényi (*5*) adds to activity the extent of multiple hydrogenolysis and the preference for cleavage of terminal or medial bonds. Mo/Al_2O_3 is intermediate in the degree of multiple hydrogenolysis. Platinum and palladium are at the extreme of giving only single hydrogenolysis, whereas iron at the other extreme gives primarily methane as the product of hydrogenolysis of higher alkanes. Palladium heavily favors the cleavage of terminal bonds, whereas iridium favors that of medial bonds (*5*). Mo/Al_2O_3 leads to the cleavage of all bonds but with a preference for the cleavage of terminal bonds rather like that of rhodium.

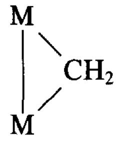
Mechanism

Pathways by all conceivable mechanisms for hydrogenolysis which do not violate some fundamental physical principle must proceed at a finite rate (*11*), but many of these pathways will be extremely slow. It is of interest to consider some processes for C—C bond formation which appear to be reasonably well established, since microscopic reversibility implies that the reverse of these processes should have a finite rate leading to hydrogenolysis. Most of these cases involve reactions of organometallic complexes, and, of course, still other mechanisms might well occur on the surfaces of metals. Among the mechanisms established for organometallic complexes are:

(i) The carbene insertion reaction (*12*, *13*),

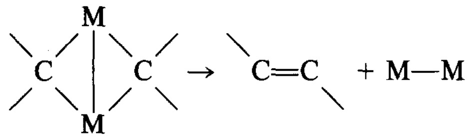


or its equivalent with

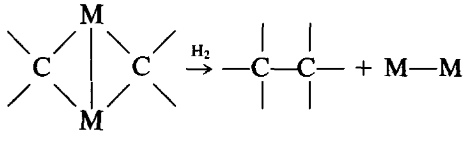


rather than $M{=}CH_2$ (*14*, *15*). The forward process is a step in the currently favored mechanism for the Fischer–Tropsch reaction. Osterloh *et al.* have proposed the retrocarbene insertion reaction as the mechanism of the hydrogenolysis of linear alkanes (*16*), but Rooney (*17*) had earlier proposed this reaction for the hydrogenolysis of neopentane.

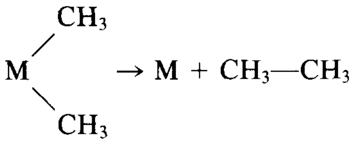
(ii) The carbene coupling reaction (*18*, *19*),



and

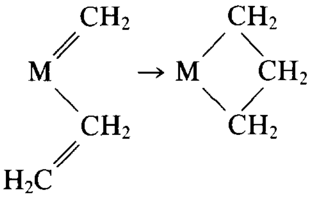


(iii) Reductive elimination of alkyl groups is well established, for example, with methyl groups (*20*),



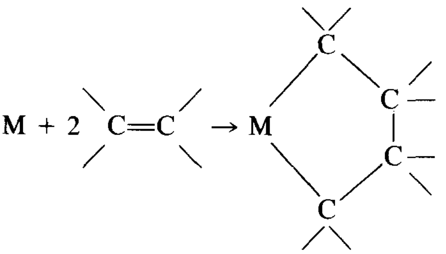
This could suggest that direct dissociative adsorption of less hindered alkanes with cleavage of a C—C bond might have N_t's larger than 1.0 per megayear.

(iv) Formation of metallocyclobutanes as in the Chauvin–Hérisson mechanism for olefin metathesis,



The reverse of this reaction from an α,γ-diadsorbed alkane has been suggested by Rooney as a likely mechanism for the hydrogenolysis of certain alkanes (*17*).

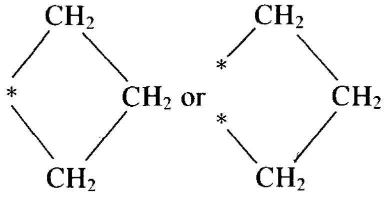
(v) Formation of a metallocyclopentane from two molecules of adsorbed olefin (*21*),



More than one of the above processes or of still others is likely to occur at a significant rate with many alkanes. Note that only (i), (ii), and (iii) could be involved with ethane, (iv) needs a three-carbon chain, and (v) needs a four-carbon chain. The latter is particularly attractive for the hydrogenolysis of hexamethylethane on platinum where initial cleavage to two molecules of isobutane predominates and proceeds relatively rapidly (*22*).

Initial cleavage of methane from carbon atom-2 in 2,2-dimethylpropane (neopentane) and 2,2-dimethylbutane (neohexane) cannot involve an initial adsorbed intermediate in which carbon atom-2 is bonded to the surface as, for example, in the reverse of mechanism (ii) or in an analogous mechanism starting from *–C–C–* or the like. Mechanism (iv) is attractive here and (v) is of interest for medial cleavage in neohexane, but mechanism (i) is also conceivable. Further work would be needed to provide more specific mechanistic details for hydrogenolysis on $Mo(0)/Al_2O_3$.

The hydrogenolysis of cyclopropane is a special case. On $Mo(0)/Al_2O_3$ it is several times faster than that of propane and single, double, and triple hydrogenolyses are involved at 250°C. At 100°C, hydrogenolysis of cyclopropane is fast, but that of propane is negligible (*23*). One would expect initial cleavage of cyclopropane to give



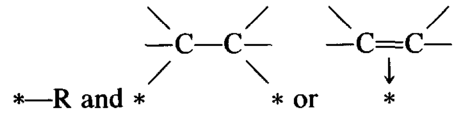
which could then react directly to form propane or which could undergo further cleavage by mechanism (iv). It would seem that at 250°C the rate of formation of the immediate precursor or precursors of hydrogenolysis are only several times faster from cyclopropane than from propane.

Table 6 shows values of N_t for the hydrogenolysis of cyclopropane at 300°C on catalyst P1 which started near MoO_3/Al_2O_3 and which was then treated H_2,450° (av ON $\cong$ 4), H_2,650° (av ON $\cong$ 2), and H_2,950° (av ON = 0). As the temperature of pretreatment by hydrogen was increased, N_t for hydrogenolysis varied little, but the extent of multiple hydrogenolysis rose dramatically. On the other hand, N_t for the hydrogenolysis of propane rose rapidly with the pretreatment temperature (Table 1) in parallel to the increase in the degree of multiple hydrogenolysis of cyclopropane. Further, carbon monoxide poisoned the hydrogenolysis of propane to a much greater extent than that of cyclopropane (P3 in Table 6). Apparently, cyclopropane reacts with Mo^{4+}, Mo^{2+}, and Mo(0) at roughly the same rate at 300°C as is also true at 100°C (*23*), but the direct hydrogenolysis of metallocyclobutane must be fast vs cleavage as in (iv) on Mo^{4+} and Mo^{2+}. This poses the problem that Mo^{2+} is a much better catalyst for the metathesis of olefins than Mo(0) at 0–100°C. Perhaps, $*{=}CH_2$ + diadsorbed ethane (or adsorbed ethylene) is relatively more stable vs metallocyclobutane on Mo(0). Rapid metathesis would require the two to have roughly equal Gibbs energies.

Pulses of butenes hydrogenate rapidly at 250°C, but conversion to hydrogenolytic products is about the same as in pulses of butane. One could conclude that intermediates in

$$H_2 + \text{butene} \rightarrow \text{butane}$$

are not ones which lead directly to hydrogenolysis, i.e., presumably



However, the rapidity of isotope exchange between D_2 and alkanes at 20°C (*24*) could indicate that $RH + 2* \rightarrow R* + H*$ is fast and in equilibrium at 250°C and that $[R*]$ would be nearly the same during runs with butane and butenes. Measurement of isotopic exchange during the hydrogenolysis of butane by D_2 at 250°C might help elucidate this question.

REFERENCES

1. Nakamura, R., Pioch, D., Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **93,** 388 (1985).

2. Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **63,** 463 (1980).

3. Maire, G., Zahraa, O., Garin, F., Crouzet, C., Aeiyach, S., Legare, P., and Braunstein, P., *J. Chim. Phys. Phys.-Chim. Biol.* **78,** 951 (1981).

4. Zimmer, H., Tétényi, P., and Paál, Z., *J. Chem. Soc., Faraday Trans. 1* **78,** 3573 (1982).

5. Paál, Z., and Tétényi, P., *Catalysis* (*London*) **5,** 80 (1982).

6. Montarnal, R., and Martino, G., *Rev. Inst. Fr. Pet.* **32,** 367 (1977).

7. Galvagno, S., Schwank, J., Gubitosa, G., Tauszik, G. R., *J. Chem. Soc., Faraday Trans. 1* **78,** 2509 (1982).

8. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 253 (1979).

9. Kikuchi, E., Tsurumu, M., and Morita, Y., *J. Catal.* **22,** 226 (1971).

10. Foger, K., and Anderson, J. R., *J. Catal.* **59,** 325 (1979).

11. Burwell, R. L., Jr., and Pearson, R. G., *J. Phys. Chem.* **70,** 300 (1966).

12. Hayes, J. C., and Cooper, N. J., *J. Amer. Chem. Soc.* **104,** 5570 (1982).

13. Grubbs, R. H., and Miyashita, A., *J. Amer. Chem. Soc.* **100,** 7418 (1978).

14. Sumner, C. E., Jr., Collier, J. A., and Pettit, R., *Organometallics* **1,** 1350 (1982).

15. Theopold, K. H., and Bergman, R. G., *J. Amer. Chem. Soc.* **103,** 2489 (1981).

16. Osterloh, W. T., Cornell, M. E., and Pettit, R., *J. Amer. Chem. Soc.* **104,** 3759 (1982).

17. Rooney, J. J., *J. Catal.* **58,** 334 (1979).

18. Laws, W. J., and Puddephatt, R. J., *J. Chem. Soc., Chem. Commun.*, 116 (1984).

19. Cooke, M., Davies, A. L., Guerchais, J. E., Knox, S. A. R., Mead, K. A., Roué, J., and Woodward, P., *J. Chem. Soc., Chem. Commun.*, 862 (1981).

20. Braterman, P. S., and Cross, R. J., *Chem. Soc. Rev.* **2,** 271 (1973).

21. McLain, S. J., Sancho, J., and Schrock, R. R., *J. Amer. Chem. Soc.* **102,** 5610 (1980); Grubbs, R. H., and Miyashita, A., *J. Amer. Chem. Soc.* **100,** 1300 (1978).

22. Leclercq, G., Leclercq, L., and Maurel, R., *Bull. Soc. Chim. Belg.* **88,** 599 (1979).

23. Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **88,** 388 (1984).

24. Defossé, C., Laniecki, M., and Burwell, R. L., Jr., *Proc. Int. Congr. Catal.* **7,** 1331 (1980).