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Reactions of Hydrocarbons over Ru/SiO$_2$: Exchange with Deuterium and the Onset of Hydrogenolysis

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Exchange reactions with deuterium of a number of hydrocarbons, chosen to provide evidence about the nature of the intermediates, have been followed mass spectrometrically over a ruthenium–silica catalyst. The selected hydrocarbons were methane, propane, 2-methylpropane (2MP), 2,2-dimethylpropane (DMP), and 2,2,3,3-tetramethylbutane (TMB). Products from the reaction of propane and 2MP were analysed by deuterium NMR spectroscopy. The extent of multiple exchange increased with temperature and mechanisms involving $\alpha\alpha$- or $\alpha\delta$-adsorbed intermediates were favoured.

The hydrogenolyses of DMP and TMB were followed at higher temperature with emphasis on the selectivity of the reaction and the change of the pattern of products with contact time. Subsidiary experiments to learn more about the course of the reactions with TMB were carried out with 2,2,3-trimethylbutane (TriMB) and 2,3-dimethylbutane (23DMB).

There was evidence for a strong hydrocarbon–ruthenium interaction leading to a sequence of events with increase of temperature, relatively easy exchange but with self-poisoning, followed by moderately easy hydrogenolysis, again subject to self-poisoning. The sequence suggested the formation in turn of reversibly adsorbed hydrocarbon intermediates, more strongly adsorbed species leading to hydrogenolysis and finally carbonaceous residues.

Ruthenium has been shown by Sinfelt[1] to be one of the most effective metals for hydrogenolysis of hydrocarbons with an activity greater than rhodium for the reaction of ethane and *n*-heptane. Machiels and Anderson[2] also reported that for the hydrogenolysis of propane, hexane and 2,2-dimethylbutane the order of activity was Ru > Co > Ni > Fe. Recently, Coq *et al.*[3] have investigated the influence of dispersion on the behaviour of a series of Ru/Al$_2$O$_3$ catalysts for the hydrogenolysis of a number of hydrocarbons. Similar studies have been carried out by Bond *et al.*[4] for the reaction of propane and *n*-butane, and for these molecules hydrogenolysis was detected at temperatures as low as 390 K.

In contrast to the results for hydrogenolysis of hydrocarbons on ruthenium, relatively little has been reported on the exchange of hydrocarbons with deuterium. Early work[5] showed that ruthenium films were active for ethane exchange, giving twin-peaked distributions similar to those for platinum, in the temperature range from 273 to 323 K but the results were rather irreproducible. Methane exchange has been studied[6] on a 3% Ru/SiO$_2$ catalyst at 398 K and at this which temperature 2,2-dimethylpropane (DMP) underwent hydrogenolysis at *ca.* 25% of the rate of the methane exchange. The exchange of both methane and cyclopentane have been studied by van Broekhoven and Ponec[7] on various silica-supported metals including ruthenium. They obtained evidence that metals with a high activity for hydrogenolysis tended to show more evidence of intermediates with metal–carbon multiple bonds. The exchange of cyclopentane over ruthenium was examined in the temperature range from 270 to 400 K but there was evidence of some hydrogenolysis at 328 K and by 374 K the rate of hydrogenolysis was *ca.* 20% of the rate of exchange.

The first objective of the present work was to investigate exchange reactions of a series of hydrocarbons on silica-supported ruthenium. We expected that the temperature range for studying these reactions might be rather limited because of the comparatively low temperatures at which hydrogenolysis becomes feasible over ruthenium. For the same reason we were prepared to find evidence of some self-poisoning of the exchange reactions due to the formation of strongly adsorbed species which would become intermediates for hydrogenolysis. This type of behaviour has been reported[8] for the exchange of various hydrocarbons containing quaternary carbon atoms over silica-supported rhodium and attributed to the fact that rhodium is an active hydrogenolysis catalyst. The choice of hydrocarbons was dictated by the possibility of obtaining evidence for the various types of adsorbed intermediates responsible for the exchange processes and which at higher temperatures might lead on to hydrogenolysis. Methane was of interest since multiple exchange requires the formation of the $\alpha\alpha$-diadsorbed (carbene) species. Propane and 2-methylpropane (2MP) were used because deuterium NMR analysis of the products can provide evidence[9] for the contributions of $\alpha\alpha$- and $\alpha\gamma$-adsorbed species in addition to the common $\alpha\beta$-adsorbed intermediates involved in the multiple exchange processes with many hydrocarbons. We also selected DMP and 2,2,3,3-tetramethylbutane (TMB) for study because they cannot form $\alpha\beta$-adsorbed species but can undergo differing extents of multiple exchange which can be related to the formation of $\alpha\alpha$-, $\alpha\gamma$-, or $\alpha\delta$-adsorbed intermediates.[8] With such molecules, four processes have been identified. Process I is stepwise exchange involving the reversible formation of adsorbed alkyl intermediates. Process II is multiple exchange but limited to a single methyl group and is associated with the initial production of D$_2$- and D$_3$-compounds; it corresponds closely to the multiple exchange of methane. Process III involves interconversion of alkyl and $\alpha\gamma$-adsorbed intermediates and is responsible for the production of isotopic products from DMP giving fragment ions in the range from D$_4$- to D$_9$-. Process III could also give rise to D$_2$- and D$_3$-products but the evidence suggests that these arise largely from process II. With TMB, initial products exchanged in more than three methyl groups require the interconversion of alkyl and $\alpha\delta$-adsorbed species and this is process IV. Fragment ions containing 10 to 15 deuterium atoms from the initial products from the exchange of TMB are evidence for process IV. Ions in the range from D$_4$ to D$_9$ may arise from either process III or process IV.

Preliminary investigation showed that at the higher end of the temperature range used to study the exchange of DMP and TMB, hydrogenolysis was also occurring. Consequently, an investigation of these reactions was made with particular emphasis on the analysis of the products formed in order to attempt to relate the mechanisms of hydrogenolysis to intermediates responsible for exchange. In order to understand the sequence of events involved in the hydrogenolysis of TMB, experiments with 2,2,3-trimethylbutane (TriMB) and 2,3-dimethylbutane (23DMB) were also carried out.

Experimental

Materials

The catalyst used in these experiments was the 100% Ru of the Ru–Cu bimetallic series previously prepared by Rouco *et al.*[6] It contained 2.97×10^{-4} mol Ru g^{-1} (SiO_2) and had a metallic dispersion of 65% as measured by hydrogen chemisorption. Methane (99.97%), propane, DMP (99%), 2MP and deuterium (99.5%) were supplied by Matheson Gas Products; TMB (99%) was obtained from the Aldrich Chemical Co., and 23DMB (99.5%) from Fluka Ltd. The source of the TriMB was unknown but proved to be $>99\%$ pure by gas chromatography. Apart from some further purification by freezing and pumping prior to use the hydrocarbons were used as received, the deuterium was purified by diffusion through a heated Pd–Ag alloy thimble. Hydrogen (B.O.C. Ltd.) used for catalyst reduction was passed through a Deoxo unit and two molecular sieves, one at ambient and the other at liquid-nitrogen temperature.

Catalytic Reactor

The hydrocarbon reactions were carried out in an all-glass recirculating system similar to that described by Bird *et al.*[10] The system was connected *via* a capillary leak to a VG Micromass (MM601) mass spectrometer and by a gas-sampling valve to a Perkin-Elmer F33 gas chromatograph. The total volume of the system was 360 cm^3. The charge of hydrocarbon was normally 0.83 kPa which corresponded to 8×10^{19} molecules with an 8 : 1 ratio of deuterium : hydrocarbon. For the experiments involving subsequent analysis by deuterium NMR a higher pressure of hydrocarbon of 2.5 kPa was required and this necessitated a lower ratio of deuterium : hydrocarbon of 5 : 1. Prior to each experiment a fresh sample of catalyst was purged with hydrogen for 20 min at room temperature and then the temperature was raised at 10 K min^{-1} to 623 K where it was reduced in flowing hydrogen for 1 h. The catalyst was evacuated at this temperature for a further hour before decreasing to the required temperature.

Exchange

The isotopic analyses were made using low accelerating voltages for the ionising electrons in order to minimise fragmentation; for propane and 2MP the value used was 18 eV, the analysis of the latter was made in terms of the fragment ion $C_3X_7^+$ (X representing H or D). The quaternary hydrocarbons were ionised with 35 eV electrons and analysed as the pseudo-parent ions $C_4X_9^+$ and $C_7X_{15}^+$ for DMP and TMB, respectively. A small correction had to be made to the TMB exchange data at *m/z* 114, corresponding to the product ion ($C_7D_{15}^+$), for the occurrence of a small amount of the parent ion $C_8H_{18}^+$. The methane was ionised using 20 eV electrons and corrections had to be made for the water background in the mass spectrometer. Initially the background gave peaks in the range of *m/z* from 16 to 18 but there was a subsequent increase of the peaks 19 and 20 due to exchange of the water in the spectrometer with deuterium. However, the combined total of the background peaks diminished with time as the reactant gases were allowed to leak into the mass spectrometer but reached approximately steady values after *ca.* 30 min. Consequently, for each experiment the reaction mixture was allowed to bleed into the spectrometer for this period before exposing it to the catalyst and the size of the background peaks then determined and used to correct the observed peaks in the range of *m/z* from 18 to 20 during the subsequent exchange of methane. Reasonably accurate analyses of the isotopic methanes throughout the course of the exchange reaction were thus obtained. For each experiment the peak heights were corrected for naturally occurring isotopes and for fragmentation, the results were then plotted according to the reversible first-order equation[11] for the disappearance of the parent or pseudo-parent ions;

$$-\ln(x - x_\infty) = kt/(100 - x_\infty) - \ln(100 - x_\infty) \tag{1}$$

in which x is the percentage of the light ion at time t, $x_\infty (\approx 0)$ is the value at equilibrium and k is the initial rate (in % $time^{-1}$). The initial product distributions were derived from plots of percentage D_n species *vs.* the percentage of the light ion reacted. The value of M, the mean number of deuterium atoms entering each molecule under initial conditions, was obtained from

$$M = \sum_i iD_i \tag{2}$$

where D_i is the amount of the initial product with i deuterium atoms. The technique for collecting the hydrocarbon samples and for analysing them subsequently by deuterium NMR spectroscopy has been described.[12]

Hydrogenolysis

The hydrogenolysis products were separated in the gas chromatograph using a 4 m × 3 mm stainless-steel column containing 15% w/w OV101 on Chromosorb W (80–100 mesh) and detected with a flame ionisation detector. Using a temperature programme of ambient for 8 min followed by heating to 393 K at 15 K min^{-1} with a nitrogen backing pressure of 156 kPa the following hydrocarbons were separated; (abbreviations and retention times in min are indicated in parentheses) methane (C_1; 2.6), ethane (C_2; 2.9), propane (C_3; 3.6), 2-methylpropane (2MP; 4.8), 2,2-dimethylpropane (DMP; 6.4), 2-methylbutane (2MB; 9.0), 2,2-dimethylbutane (22DMB; 11.0), 2,3-dimethylbutane (23DMB; 12.5), 2,2-dimethylpentane (22DMP; 15.4), 2,2,3-trimethylbutane (TriMB; 16.0), 2,2,3,3-tetramethylbutane (TMB; 19.2). The course of the reaction was followed by the decrease in the concentration of the reactant expressed as a percentage of the total carbon present in the vessel. The selectivities for each product were detemined by plotting the amount formed against the amount of reactant destroyed and measuring the initial gradients. The depth of hydrogenolysis, M_b, was obtained from the relation

$$M_b = \left[\sum_i S_i/(1 - S_{\text{isom}})\right] - 1 \tag{3}$$

where S_i are selectivities for hydrogenolysis products and S_{isom} is the selectivity for isomerisation. A value of M_b of unity shows a stepwise hydrogenolysis with the cleavage of only one C—C bond for each molecule of reactant destroyed.[13]

Results

Exchange

Methane

Methane exchange was investigated at temperatures of 400, 431 and 473 K. As shown in Fig. 1, at these temperatures

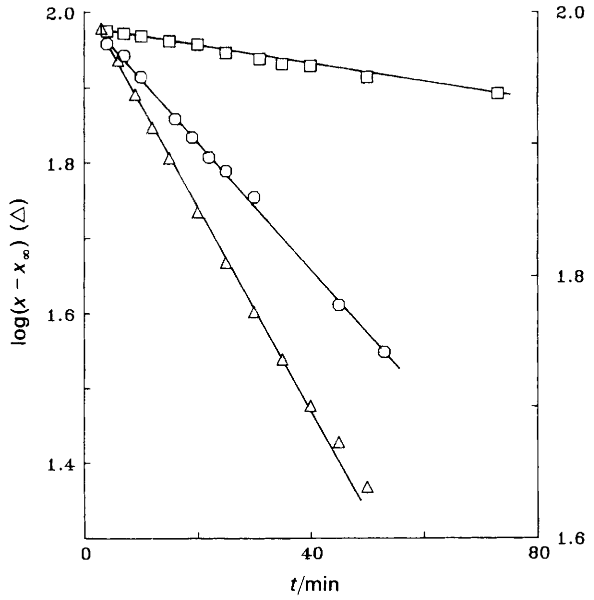


Fig. 1 Rate plots according to eqn. (1) for methane exchange over Ru/SiO_2 : 400 K (□), 431 K (○) and 473 K (△)

Table 1 Initial product distributions in methane exchange with deuterium over Ru/SiO_2

	initial product distribution				
temperature/K	D_1	D_2	D_3	D_4	M
400	0.94	—	—	0.06	1.18
431	0.80	—	—	0.20	1.60
473	0.60	0.05	0.04	0.31	2.06
Rh/SiO_2[a]					
440	0.77	0.07	0.03	0.13	1.52

[a] Ref. 14.

linear rate plots with time were found; however, at the highest temperature the plot does show some curvature after 60% reaction. At 400 and 431 K there was little or no formation of CH_2D_2 and CHD_3, as indicated in Table 1.

2,2-*Dimethylpropane and* 2,2,3,3-*Tetramethylbutane*

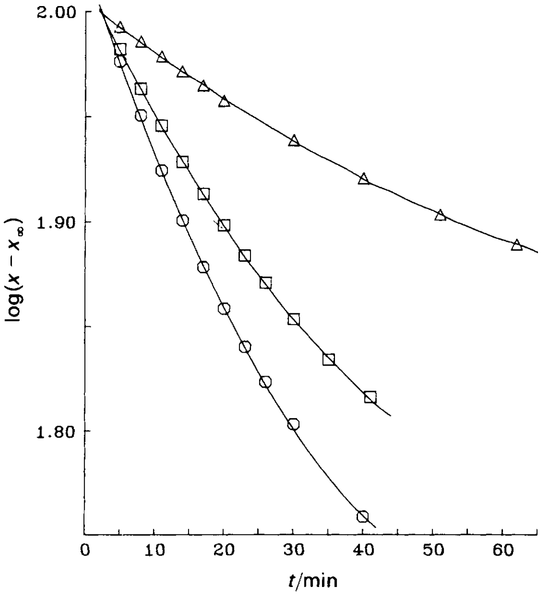


Fig. 2 Rate plots according to eqn. (1) for 2,2-dimethylpropane exchange over Ru/SiO_2: 364 K (△), 400 K (□) and 430 K (○). The points are experimental data with the 2nd degree polynomial fit being shown by the curves

Table 2 Results for 2,2-dimethylpropane exchange over Ru/SiO_2

catalyst	Ru	Ru	Rh[a]	Ru	Ru
temperature/K	341	364	393	400	430
$10^2\ r_0$/molecule s^{-1} (Ru atom)$^{-1}$	0.24	0.86	1.32	3.69	6.13
r_{30}/r_0	0.89	0.74	0.76	0.59	0.47
initial product distribution as $C_4X_9^+$ ions					
D_1	0.828	0.835	0.680	0.596	0.276
D_2	0.090	0.120	0.130	0.225	0.133
D_3	0.072	0.036	0.095	0.104	0.162
D_4	0.010	0.006	0.036	0.046	0.106
D_5		0.002	0.017	0.021	0.079
D_6			0.012	0.009	0.071
D_7			0.010		0.065
D_8			0.010		0.061
D_9			0.010		0.047
M	1.26	1.22	1.77	1.70	3.64

[a] Ref. 8.

Table 3 Results for 2,2,3,3-tetramethylbutane exchange over Ru/SiO_2

catalyst	Ru	Ru	Ru	Rh[a]	Ru	Ru
temperature/K	323	350	364	394	399	463
$10^2\ r_0$/molecule s^{-1} (Ru atom)$^{-1}$	0.06	1.06	1.99	0.89	2.59	2.64
r_{30}/r_0	0.75	0.58	0.72	0.90	0.63	0.64
initial product distribution as $C_7X_{15}^+$ ions						
D_1	0.893	0.755	0.694	0.643	0.507	0.33
D_2	0.076	0.117	0.157	0.136	0.154	0.11
D_3	0.031	0.057	0.057	0.042	0.074	0.07
D_4		0.017	0.018	0.014	0.043	0.04
D_5		0.008	0.011	0.007	0.037	0.03
D_6		0.005	0.009	0.004	0.039	0.02
D_7		0.004	0.010	0.004	0.038	0.03
D_8		0.004	0.010	0.007	0.035	0.04
D_9		0.010	0.010	0.022	0.028	0.05
D_{10}		0.003	0.008	0.011	0.019	0.05
D_{11}		0.004	0.006	0.014	0.013	0.06
D_{12}		0.010	0.004	0.027	0.007	0.06
D_{13}		0.002	0.002	0.017	0.003	0.04
D_{14}		0.001	0.001	0.024	0.001	0.04
D_{15}		0.003	0.001	0.032	0.001	0.04
M	1.14	1.66	1.85	3.06	2.91	5.7

[a] Recalculated from ref. 8.

DMP and TMB exchange with deuterium were investigated in the temperature ranges 341–430 K and 323–463 K, respectively. At all temperatures there was a marked decrease in the rates of reaction with time. In order to obtain initial rates, r_0, a second-degree polynomial was fitted to the results and examples are shown in Fig. 2 for reactions of DMP at 364, 400 and 430 K. A further rate after 30 min, r_{30}, was also calculated and the ratios of the rates r_{30}/r_0 are reported in Tables 2 and 3 to show the degree of self-poisoning in the various experiments. The patterns of isotopic products expressed as percentage D_i formed against D_0 reacted were not affected by the poisoning. An example for TMB exchange at 399 K is given in Fig. 3 and the initial product distributions were easily obtained from the slopes of the lines, despite the self-poisoning revealed by the inset. Tables 2 and 3

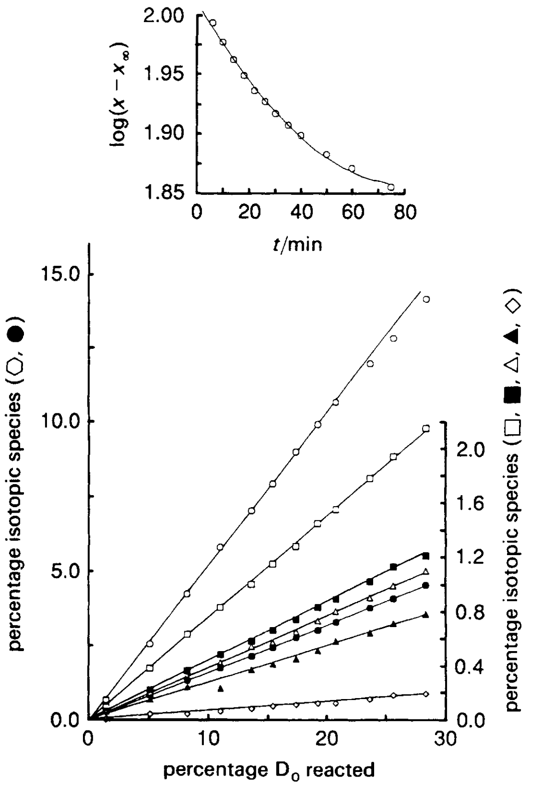


Fig. 3 Exchange of 2,2,3,3-tetramethylbutane at 399 K. Selected values of D_i formed plotted against D_0 reacted; D_1 (○); D_2, (●); D_3, (□); D_4, (■); D_6, (△); D_9, (▲); D_{12}, (◇). Above: rate plot according to eqn. (1)

contain the initial product distributions for DMP and TMB, respectively, as well as other experimental data. Results over a Rh/SiO_2 catalyst previously reported[8] are also given for comparison.

Methane gave a linear Arrhenius plot, Fig. 4. The overall activation energy was 85 ± 4 kJ mol^{-1}. This could be further sub-divided into activation energies for process I, E_I, and process II, E_{II}, Table 4. Process I is simple stepwise exchange resulting in formation of CH_3D and process II is the multiple-exchange process giving the products CH_2D_2, CHD_3 and CD_4.

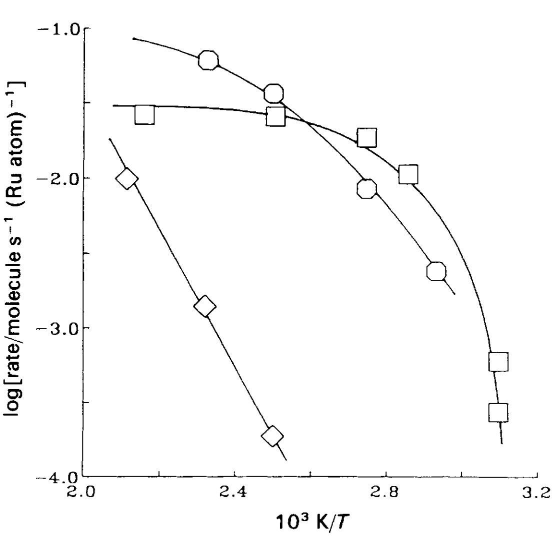


Fig. 4 Arrhenius plots for exchange over Ru/SiO_2: methane (◇), 2,2-dimethylpropane (○) and 2,2,3,3-tetramethylbutane (□)

Table 4 Activation energies (kJ mol^{-1}) of exchange processes for methane, 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane

reactant	metal	E_I	E_{II}	E_{II-I}	E_{III-I}	E_{IV-I}
CH_4	Ru	72	120	—	—	—
	Rh[a]	66	94	—	—	—
DMP	Ru	—	—	24	69	—
	Rh[b]	—	—	18	39	—
TMB	Ru	—	—	19	—	42
	Rh[c]	—	—	10	—	38

[a] Ref. 14; [b] ref. 15; [c] ref. 16.

Owing to the self-poisoning which occurred during the exchange of DMP and TMB, which was more obvious at the higher temperatures, the Arrhenius plots for these two molecules were non-linear, Fig. 4, and estimation of the overall activation energies was not possible. However, as the initial product distributions were not affected by the self-poisoning it was possible to estimate the differences of activation energy between the various processes for exchange by making Arrhenius plots for the ratio of the relevant products. Thus for both reactants, the difference in activation energy between process II (methyl group multiple exchange) and process I (stepwise exchange), *i.e.* $E_{II} - E_I$, was obtained from the plot of $\log[(D_2 + D_3)/D_1]$ against $1/T$. For DMP exchange involving more than one methyl group and occurring by process III (interconversion between adsorbed alkyl radicals and $\alpha\gamma$-adsorbed species) giving rise to $C_4X_9^+$ containing four or more deuterium atoms, an estimate of $E_{III} - E_I$ was obtained from a plot of $\log(\sum_4^9 D_i/D_1)$ against $1/T$. With TMB, the exchange of methyl groups attached to both the quarternary carbon atoms necessitates process IV (interconversion between adsorbed alkyl radicals and $\alpha\delta$-adsorbed species). Products giving fragment ions, $C_7X_{15}^+$, with from four to nine deuterium atoms could be formed by process III or process IV but the presence of ions with 10 or more deuterium atoms was evidence that process IV operated. As an approximation with TMB we neglected the possible contribution from process III and obtained a measure of $E_{IV} - E_I$ from a plot of $\log(\sum_4^{15} D_i/D_1)$ against $1/T$. The Arrhenius plots to determine these differences in activation energy are given in Fig. 5 and the derived values in Table 4.

Propane and 2-Methylpropane

Exchange reactions were carried out with propane and 2MP principally to obtain information about the isotopic products by deuterium NMR spectroscopy in addition to mass spectrometry. Propane exchanged readily over Ru/SiO_2 at 294 K with an initial rate of 1.45×10^{-2} molecule s^{-1} (Ru atom)$^{-1}$ but the rate had fallen by 26% after 30 min. A sample was collected for NMR analysis after 15.3% exchange with distribution of products shown in Table 5. The NMR spectrum is shown in Fig. 6 and relative percentages of deuterium in the various groupings are given in Table 6. 2-Methylpropane exchanged at 273 K with an initial rate of 3.21×10^{-2} molecule s^{-1} (Ru atom)$^{-1}$ but the rate had fallen by 71% after 30 min. Deuterium NMR analysis was carried out on a sample collected from a run at 298 K which gave an initial rate of *ca.* 8×10^{-2} molecule s^{-1} (Ru atom)$^{-1}$. The mass spectrometric analysis of the sample is given in Table 5. The most useful information from the NMR analysis was that the ratio of primary deuterium: tertiary deuterium was 3.65 : 1 and that the percentage of primary deuterium present in the groupings of CD_3CH— and CD_3CD— were 11.6 and 27.5, respectively, *i.e.* the percentage of CD_3CH— in CD_3CX— was 30%. No hydrogenolysis was detected during the exchange of either propane or 2MP.

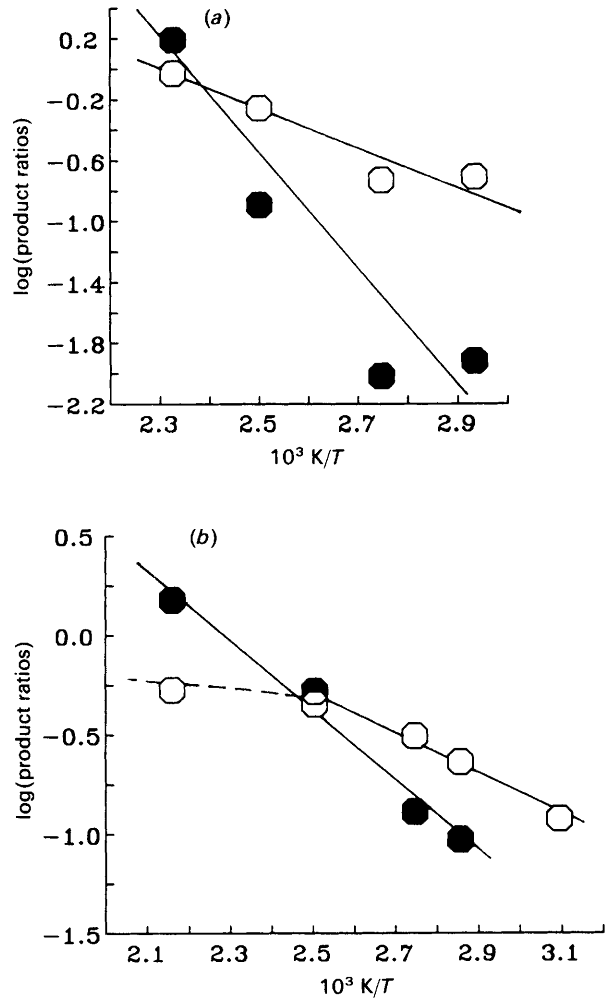


Fig. 5 Arrhenius plots of product ratios to determine differences in activation energy for various processes: (*a*) 2,2-dimethylpropane; $E_{II} - E_I$ (○); $E_{III} - E_I$, (●); (*b*) 2,2,3,3-tetramethylbutane: $E_{II} - E_I$, (○); $E_{IV} - E_I$ (●)

Hydrogenolysis

At the higher temperatures investigated in the exchange reactions some hydrogenolysis activity of DMP and TMB was also detected. The less reactive molecule was DMP where only 0.5% hydrogenolysis occurred after 150 min at 400 K and *ca.* 2% at 430 K in a similar time period. As with exchange the disappearance of the reactants with time was non-linear, Fig. 7, but a least-squares approximation by a second-degree polynomial proved to be adequate to describe the data at 399 and 430 K for all the reactants. The products from the reaction of TMB at 430 and 463 K are shown in Fig. 8 and 9, respectively. The inset in Fig. 9 shows the inade-

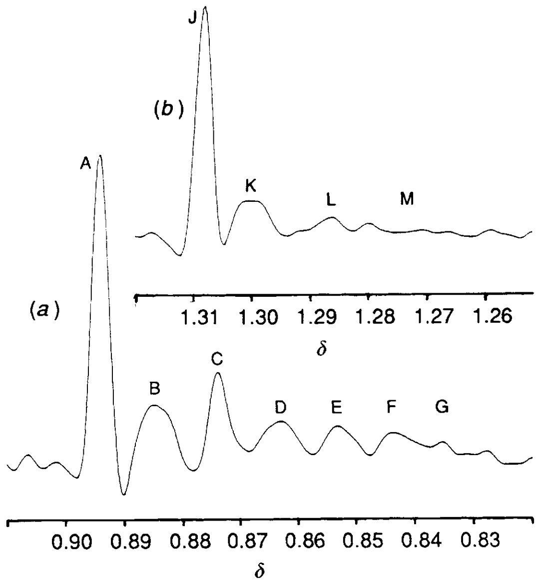


Fig. 6 Deuterium NMR spectra for propane; (*a*) primary deuteriums, (*b*) secondary deuteriums

Table 6 Deuterium NMR analyses of exchanged propanes

resonances	grouping	isotopic shifts	D (%)
primary deuterium			
A	CH_2DCH_2-	0	23
B	CH_2DCHD-	β	9
C	CH_2DCD_2- CHD_2CH_2-	2β α	9
D	CHD_2CHD-	$\alpha + \beta$	8
E	CHD_2CD_2- CD_3CHD-	$\alpha + 2\beta$ 2α	6
F	CD_3CHD-	$2\alpha + \beta$	11
G	CD_3CD_2-	$2\alpha + 2\beta$	
secondary deuterium			
J	$CHD(CH_3)_2$	0	20
K	$CHD(CH_2D)(CH_3)$	β	7
L	various	2β or α	4
M	various	$>2\beta$ or $>\alpha$	3

Table 5 Mass spectrometric results for samples of exchanged propanes and 2-methylpropanes taken for NMR analysis

composition	propane, 294 K		2-methylpropane, 298 K
	parent ions (%)	deuterium in each product (%)	fragment ions ($C_3X_7^+$) (%)
D_0	84.7	—	70.1
D_1	9.1	33	12.6
D_2	3.3	24	6.5
D_3	1.2	13	3.1
D_4	0.7	10	2.4
D_5	0.4	7	2.0
D_6	0.3	6.5	1.7
D_7	0.2	5.	1.6
D_8	0.05	1.5	—
M_x[a]	1.81		2.54

[a] M_x is the mean deuterium context of the exchanged ion.

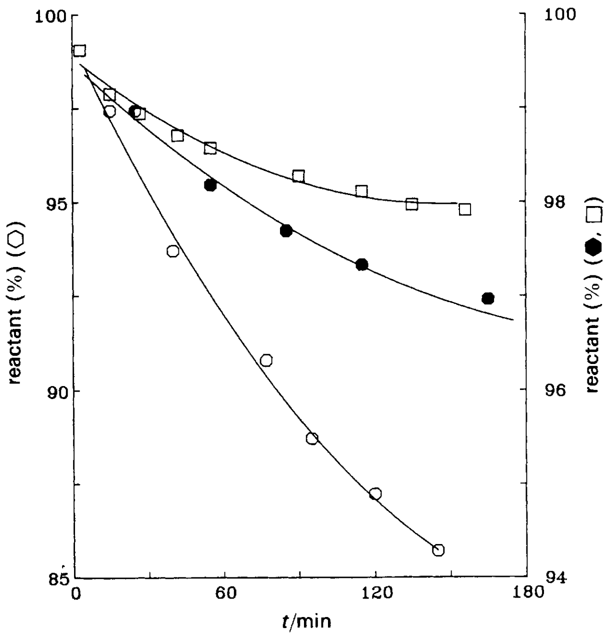


Fig. 7 Results for hydrogenolysis of 2,2-dimethylpropane at 430 K (□) and 2,2,3,3-tetramethylbutane at 400 K (●) and 430 K (○). The points are experimental data with the second-degree polynomial fit being shown by the curves

quate fit by the least-squares method at this temperature thus the rate for this experiment was obtained by drawing a tangent to the curve at 5 min. Products from the reaction of TriMB at 430 K are shown in Fig. 10. The initial products for DMP, TMB and TriMB are given with their respective rates of reaction in Table 7. The main reaction of 23DMB at 430 K was isomerisation at a rate of 3×10^{-4} molecule s^{-1} (Ru atom)$^{-1}$ and only 5% hydrogenolysis was observed after 78% of the 23DMB had reacted, see Fig. 11.

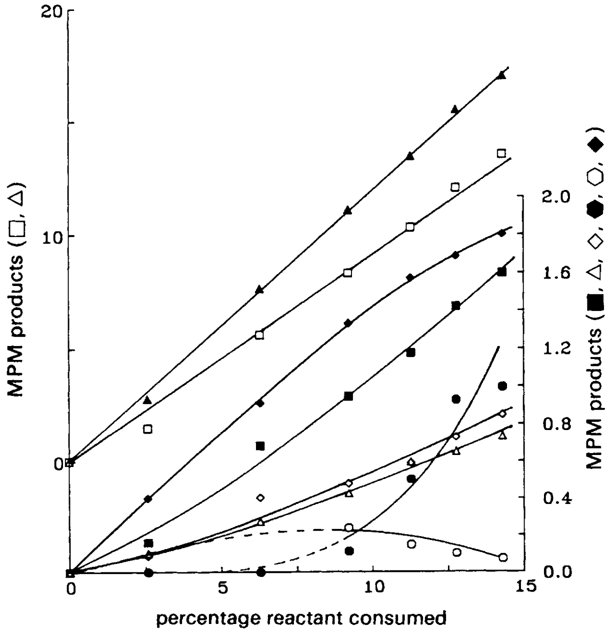


Fig. 8 Products from 2,2,3,3-tetramethylbutane hydrogenolysis over Ru/SiO_2 at 430 K: C_1 (□), C_2 (■), C_3 (△), 2MP (▲), DMP (◇), 22DMB (●), 23DMB (○), TriMB (◆). MPM represents mole of product per mole of reactant consumed

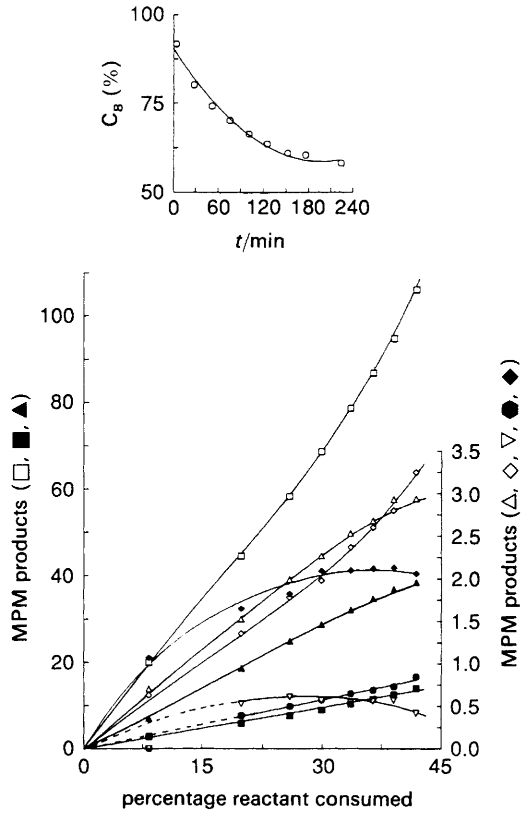


Fig. 9 Products from 2,2,3,3-tetramethylbutane hydrogenolysis over Ru/SiO_2 at 463 K. See Fig. 8 for key to symbols: 2MB (▽). Above: Disappearance of reactant with time

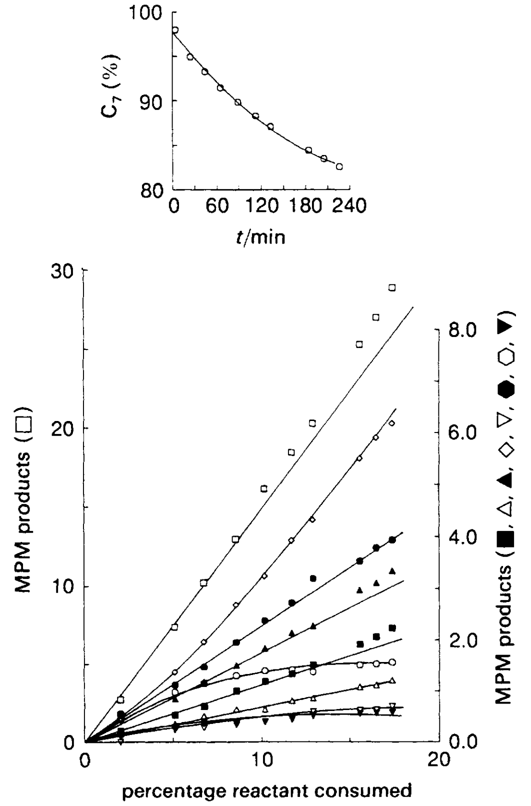


Fig. 10 Products from 2,2,3-trimethylbutane hydrogenolysis over Ru/SiO_2 at 430 K. See Fig. 8 for key to symbols: 22DMP (▼). Above: Disappearance of reactant with time

Table 7 Results for hydrogenolysis reactions over Ru/SiO$_2$

		initial products as mole per mole reactant consumed										
reactant	rate[a]	C$_1$	C$_2$	C$_3$	2MP	DMP	2MB	22DMB	23DMB	22DMP	223TriMB	M_b
DMP[b]	4.9	1.32	0.15	0.10	0.78							1.35
TMB[b]	20.4	0.93	0.10	0.05	1.20	0.05	—	—	0.03	—	0.15	1.51
TMB[c]	19.2	2.31	0.32	0.08	0.94	0.07	0.04	0.02	—	—	0.18	2.96
TriMB[b]	8.0	1.47	0.11	0.08	0.18	0.21	0.05	0.23	0.21	0.06	—	1.55

[a] 10^{-4} molecule s^{-1} (Ru atom)$^{-1}$; [b] 430 K; [c] 463 K.

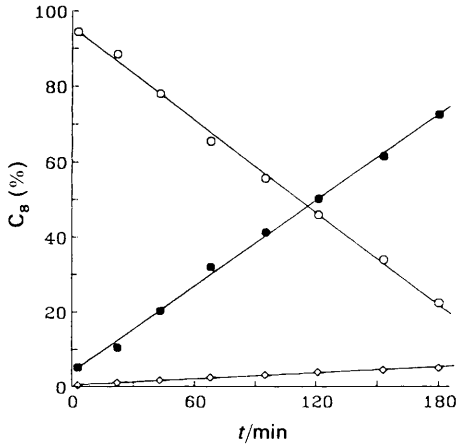


Fig. 11 Reaction profile of the reaction of 2,3-dimethylbutane over Ru/SiO$_2$ at 430 K: 23DMB (○), 22DMB (●), hydrogenolysis products (◇)

Interpretation of the NMR Spectra for Propane and 2MP

Several features of the NMR results with propane show that the multiple exchange cannot be explained simply in terms of the αβ-process (interconversion on the surface of alkyl radicals and alkene molecules) and that part must occur through interconversion of alkyl either with αα-adsorbed species or with αγ-intermediates. (*a*) If the mass spectrometric product distributions are used to calculate groupings of deuterium in a simple manner,[9] assuming that multiple exchange occurs solely by the αβ-process, too much primary deuterium is predicted for peak B and too little as peak C, in Fig. 6. This shows that some additional mechanism for multiple exchange was operating. (*b*) The shape of peak C, which is narrow, is an indication that it is mainly attributable to the grouping CHD$_2$CH$_2$— and to a lesser extent to the grouping CH$_2$DCD$_2$— which would give a broader peak due to the expected five-line spectrum (1 : 2 : 3 : 2 : 1) resulting from D–D coupling. A quantitative limit on the amount of CH$_2$DCD$_2$— can be obtained by considering the 7% of total deuterium as secondary deuterium in the isotopically shifted peaks L and M and making allowance for the contribution from the grouping responsible for peak D, CHD$_2$CHD—. This sets an upper limit of *ca.* 2% for the primary deuterium as CH$_2$DCD$_2$— and so 7% is attributable to CHD$_2$CH$_2$CX$_3$. This is direct evidence for multiple exchange by either αγ- or αα-intermediates. (*c*) The size of peak K for secondary deuterium as CHD(CH$_2$D)(CH$_3$) shows that the percentage of total deuterium in the product CH$_2$DCHDCH$_3$ is 2 × 7 = 14%. But the mass spectrometric data indicate that 24% of total deuterium occurs as D$_2$ product and so some 10% is present as either CH$_2$DCH$_2$CH$_2$D or CHD$_2$CH$_2$CH$_3$. Once again this requires a role for either αγ- or αα-intermediates or possibly both. (*d*) According to the mass spectrometric data, D$_1$-products account for 33% of the total deuterium. The size of peak J shows that 20% is attributable to CH$_3$CHDCH$_3$ and so only 13% was present as CH$_2$DCH$_2$CH$_3$. But the primary deuterium peak A corresponded to over 23% of the total deuterium and so some 10% must have come from products such as CH$_2$DCH$_2$CX$_3$ (where X is H or D). This provides unequivocable evidence for a role for αγ-intermediates.

The average deuterium content for the 2MP products can be derived from the ratio of primary : tertiary deuterium from the NMR analysis and the composition of the fragment ions formed by loss of one of the three methyl groups in Table 5. The calculated values are 2.70 primary D and 0.74 tertiary D. Furthermore, the relative sizes of the resonance corresponding to tertiary deuterium indicate that there is 0.27 D in multiply exchanged products. Clearly the αβ-process cannot be the only route to multiple exchange since it would give a tertiary deuterium in every multiply exchanged molecule. This conclusion is supported by the presence of 30% of CD$_3$CH— in the groups CD$_3$CH— and CD$_3$CD—. A simple calculation shows that the compositon of the 'deuterium' at the end of the run was $d = 0.89$ and $h = 0.11$ and so the average change of acquiring H during the experiment was only $h = 0.055$. Consequently if only the αβ-process operated for multiple exchange the percentage of CD$_3$CH— in CD$_3$CX— should have been only 5 or 6%. There must be a significant contribution from either αα- or αγ-intermediates in the multiple exchange to account for the 30% of CD$_3$CH—. Comparison with results for rhodium[9] shows that the contribution from these mechanisms is slightly higher with ruthenium than with rhodium.

Discussion

Self-poisoning

The influence of self-poisoning is substantial with ruthenium and affects both exchange of the hydrocarbons as well as hydrogenolysis. It is important to note a limitation of the value of the technique of fitting a polynomial curve to the plots of extent of reaction with time. This method does not allow for a decline in rate which is rapid compared with the times needed to analyse the reacting mixtures. It does not allow for any rapid poisoning during the first few minutes of the exposure of the reaction mixture to the metal surface. If such rapid poisoning occurs, the 'initial rates' derived from the polynomial fit will refer to a partly poisoned surface. The results in Fig. 4 illustrate this point and the marked curvature of the Arrhenius plots for the exchange of both DMP and TMB shows that the amount of rapid deactivation increases with temperature and is greater with TMB than with DMP. A similar effect occurs with hydrogenolysis; rapid self-poisoning must be invoked to account for the fact that the 'initial rate' of hydrogenolysis of TMB is lower at 463 K than at 430 K, see Table 7.

In general, the likely sequence of events as the temperature is raised with deuterium–hydrocarbon mixtures in contact with a metal catalyst is: (*a*) reversible dissociative adsorption of the hydrocarbon leading to exchange; (*b*) the formation of more strongly adsorbed species probably involving two or more carbon atoms linked to the surface; such species are less readily rehydrogenated to the original alkane so that exchange is poisoned; (*c*) increasing chance of the strongly adsorbed species undergoing carbon–carbon bond rupture giving rise to hydrogenolysis and (*d*) the formation of carbonaceous deposit on the surface by linkage of substantially dehydrogenated carbon species which reduce the activity of the surface for hydrogenolysis. On some metals such as platinum or palladium the temperature regions for this sequence of steps are widely separated so that it is possible to observe exchange at lower temperatures and hydrogenolysis at higher temperatures, both uncomplicated by significant self-poisoning. The situation with ruthenium is different; the temperature ranges for the various stages overlap and exchange and hydrogenolysis are nearly always accompanied by self-poisoning. This behaviour is a consequence of the relatively strong interaction between ruthenium and the hydrocarbons.

There are two points worth noting about self-poisoning of exchange. The results in Fig. 1 and 4 show that it does not occur with methane except to a minor extent at the comparatively high temperature of 473 K. The second is that for other hydrocarbons there is a correlation between the ease of exchange and the onset of self-poisoning. Propane and 2MP exchange readily below 300 K but show self-poisoning at these temperatures. Higher temperatures are needed to exchange DMP and TMB and the effect of self-poisoning only becomes marked at 350 K or above. The absence of any appreciable poisoning of methane exchange supports the suggestion that self-poisoning is attributable to strongly adsorbed species involving linkage of two or more carbon atoms to the surface.

Exchange of Methane, DMP and TMB

The results for methane exchange at 400 K over the ruthenium catalyst are similar to those reported previously at 398 K.[6] The product distributions are comparable and the slower rate in the present study is a consequence of inhibition of reaction by a higher pressure of deuterium. There is also a similarity between the exchange of methane over Ru/SiO_2 and results for Rh/SiO_2,[14] both in regard to product distribution and activation energy, see Table 4. The main mode of exchange over both metals at lower temperatures is process I, stepwise exchange forming CH_3D initially, but multiple exchange, process II, becomes more prominent with rise in temperature until at 473 K it accounts for 40% of the products. The major product of multiple exchange is CD_4 with only minor amounts of CH_2D_2 and CHD_3.

The principal mode of exchange of DMP over ruthenium at lower temperatures was process I, but rising amounts of D_2- and D_3-products at higher temperatures indicated an increasing contribution from process II. Products formed by process III were noticeable at 400 K and became significant at 430 K. Results over ruthenium and rhodium are similar, see Table 2, but the rate of reaction is greater with ruthenium and the contribution of process II more obvious than with rhodium.

There is more evidence of extensively exchanged products with TMB than with DMP over ruthenium. The formation of products in the range from D_{10} to D_{15}, Table 3, indicates that process IV occurs more readily with TMB than process III with DMP at 400 K. The activation energy differences in Table 4 provide further support for this statement. A comparison of the results for TMB over ruthenium at 399 K with those for rhodium at 394 K indicates that whereas both metals promote exchange by process IV, *i.e. via* $\alpha\delta$-intermediates, there are some minor differences. Exchange with rhodium tends to produce rather more of the extensively exchanged products even although the values of M for the two catalysts are close. Furthermore, the maxima at the D_9, D_{12} and D_{15}–ions with rhodium indicated a tendency to complete the exchange of reacting methyl groups and suggested a role for intermediates such as $\alpha\alpha\delta$-species.[16]

The relative rates of exchange at 364 K over ruthenium for methane, DMP and TMB were in the ratio 1 : 600 : 1300 and even at this temperature the rates for the two larger molecules may have been reduced by some rapid self-poisoning.

A comparison of the products from the exchange of propane and 2MP over ruthenium with results from earlier work with rhodium[9] shows that although there is generally less multiple exchange with ruthenium the proportion of this attributable to $\alpha\alpha$- or $\alpha\gamma$-intermediates is greater.

Hydrogenolysis

The extent of self-poisoning and particularly the evidence for some rapid deactivation of the catalyst make comparison of the rates of reaction for different molecules difficult. In the absence of poisoning, one would expect to find faster hydrogenolysis with 23DMB and TriMB than with DMP and TMB, both of which are made up of only primary and quaternary carbon atoms. But the reverse was found, suggesting that the initial rapid poisoning was more significant with the more open molecules. Thus, as with exchange, there appears to be a correlation between the ease of hydrogenolysis and the extent of self-poisoning; the degree of deactivation due to carbonaceous residues is greater with molecules which are more readily broken up. This is a reasonable conclusion. In agreement with other work over ruthenium catalysts[3,4,17] deactivation influences the rate but not the selectivities of the reactions. This suggests that the number, but not the nature, of the sites are affected. This behaviour, observed with hydrogenolysis, was also the case for the exchange experiments and is a common feature with supported-metal catalysts.[18] We, therefore, place the main emphasis on the discussion of the selectivities of the reactions rather than on the relative rates of hydrogenolysis of different compounds. Our circulating system provides more information on the sequence of reactions and the changing pattern of products with contact time than was obtainable with the conventional flow reactor used by Coq *et al.*[3] in their study of the hydrogenolysis of TMB.

The data in Table 7 for the moles of product per mole of reactant consumed show that the main reaction in the hydrogenolysis of DMP is the formation of methane and 2MP some of which undergoes further breakdown to form other products mainly by demethylation. If the propane and ethane had resulted solely from demethylation the value for methane would have been 1.43, *i.e.* $0.78 + (2 \times 0.10) + (3 \times 0.15)$, compared with the experimental value of 1.32. A comparison between the present results for the reaction DMP over ruthenium at 430 K with the behaviour of DMP over Rh/SiO_2 at 428 K[19] shows that ruthenium is slightly more reactive and gives a greater extent of multiple fragmentation, *i.e.* an M_b values of 1.35 compared to 1.10 for rhodium. There was no evidence of isomerisation over ruthenium although, as with rhodium, some of the ethane or propane could have resulted from the formation and breakdown of 2MB on the surface.

Coq *et al.*[3] have used the hydrogenolysis of TMB as a model reaction to decide on the relative importance of $\alpha\delta$- or 1,4-adsorbed intermediates leading to the splitting of the central C—C with the formation of 2MP or of $\alpha\gamma$- or 1,3-

intermediates giving rise to methane and TriMB. Our results for the reaction of TMB show that over ruthenium at 430 K the main reaction (60%) is central bond splitting to give 1.20 molecules of 2MP for each molecule of TMB disappearing. The other type of splitting to form methane and TriMB also occurred but as shown both in Table 7 and Fig. 8 and 9 further breakdown of the C_7 molecules occurs rather readily, giving rise to a number of other products as well as further methane. The experiments on the hydrogenolysis of TriMB, Fig. 10, and the reaction of 23DMB, Fig. 11, were carried out in order to elucidate the main reaction paths and the subsequent products from the reaction of the C_7 compound. The shape of the various curves in Fig. 8 to 11 are helpful in indicating how readily the products formed undergo subsequent reaction: those with a downward curvature obviously have a greater tendency to react further; those which are relatively resistant to further hydrogenolysis exhibit an upward curvature. It is useful to consider the way in which the various C_6- and C_5-compounds arise and their relative stabilities. The principal route to smaller molecules is demethylation, but some loss of C_2 or C_3 species must occur to a limited extent as well because the amounts of methane formed are not as high as would be expected if all products were the result of demethylation. In order to simplify the discussion we shall consider the formation of smaller molecules only through demethylation.

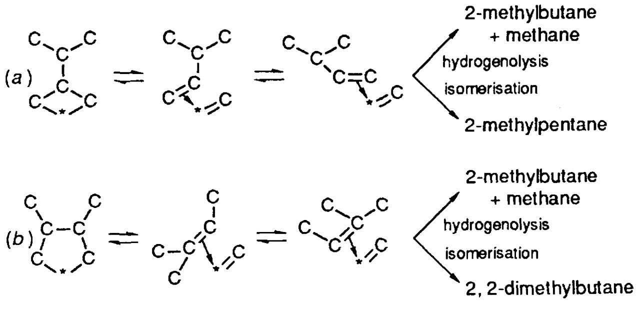
The reaction of TriMB involves some isomerisation (6%) to 22DMP and the formation of 22DMB or 23DMB. These two C_6-compounds show a remarkable difference in reactivity. The dotted curves in Fig. 8 suggest the 23DMB is rapidly converted to 22DMB which is then relatively stable. The results in Fig. 10 also show that 23DMB is the more reactive compound and its strong tendency to isomerise to 22DMB is confirmed in Fig. 11.

The main C_5-products are 2MB and DMP. Both can arise from demethylation of 23DMB, although only 2MB can be formed from 22DMB. It is not surprising that 2MB is always formed to a smaller extent than DMP and when present exhibits a downward curve, see Fig. 9 and 10. In contrast, DMP is relatively stable to further reaction and gives rising curves in each case.

Comparison of the results for the reaction of TMB at the two temperatures, Table 7, shows that increase of temperature reduces slightly the tendency to react by central C—C bond rupture and increases the extent of multiple fragmentation significantly.

Mechanistic Considerations

The exchange results demonstrate that ruthenium has a strong tendency at higher temperature to form carbene-like intermediates with multiple bonding of a carbon atom to the surface. These species are involved in the production of CD_4 from methane and the D_2- and D_3-products from DMP and TMB. These results accord with suggestions[7,20] that metals with a high activity for hydrogenolysis tend to form metal–carbon multiple bonds. The preference that ruthenium shows in the exchange reactions for process IV, involving $\alpha\delta$-intermediates, rather than process III, $\alpha\gamma$-intermediates, agrees with the main mode of hydrogenolysis of TMB by central bond cleavage as proposed by Coq *et al.*[3]



Scheme 1

The remarkable feature of the results at higher temperatures is the strong tendency for 23DMB to isomerise to 22DMB with little accompanying hydrogenolysis. Possible reaction pathways for 23DMB are shown in Scheme 1. The formation of an $\alpha\gamma$-adsorbed species, Scheme 1(*a*), might lead to isomerisation[21] to 2-methylpentane or hydrogenolysis to 2MB and methane. Alternatively, formation of the metallacyclopentane by $\alpha\delta$-adsorption would lead to either 22DMB or the same hydrogenolysis products, as shown in Scheme 1(*b*). The experimental results suggest that the second route is favoured and this accords with the preference for multiple exchange over ruthenium by $\alpha\delta$- rather than $\alpha\gamma$-intermediates. We draw attention to a difference between the behaviour of the metallacyclopentane formed by TMB and 23DMB. In the case of TMB, the absence of tertiary hydrogen may inhibit skeletal isomerisation and the preferred reaction is central bond cleavage to form two molecules of 2MP. On the other hand with 23DMB, isomerisation is the dominant reaction and there is little tendency to undergo central bond cleavage with the formation of propane.

Conclusions

A number of general points about the behaviour of hydrocarbons on ruthenium catalysts can be made on the evidence now available. (1) The metal brings about the dissociation of hydrocarbons relatively easily and so catalyses exchange of molecules with deuterium at moderately low temperatures. The relative activity of different hydrocarbons follows the usual pattern: molecules with secondary or tertiary carbon atoms > molecules with quaternary carbon atoms only > methane. (2) Rise of temperature increases the proportion of multiple exchange and mechanisms involving $\alpha\alpha$- or $\alpha\delta$-adsorbed intermediates are favoured by ruthenium. (3) Apart from methane, the exchange of hydrocarbons exhibit some extent of self-poisoning related to the formation of more strongly adsorbed species and the onset of hydrogenolysis. The degree of self-poisoning varies with the hydrocarbon but is increased as temperature is raised. (4) Ruthenium is one of the most active metals for the hydrogenolysis of hydrocarbons and the influence of the ability to form $\alpha\alpha$- and $\alpha\delta$-adsorbed species is apparent. (5) As in exchange, self-poisoning of hydrogenolysis is widespread and reflects a tendency for the formation of carbonaceous residues due to the the strong interaction of the metal with the hydrocarbons. (6) Self-poisoning leads to lower rates of reaction but does not have much influence on selectivities. This applies both in exchange and hydrogenolysis. (7) In many respects ruthenium and rhodium behave similarly for the catalysis of hydrocarbon reactions, both metals exhibiting a strong interaction with the hydrocarbons and high activity for hydrogenolysis.

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