Mechanism of Isomerization of Hydrocarbons on Metals

Part 9.—Isomerization and Dehydrocyclization of 2,3-Dimethyl[2-¹³C]pentane on a 10 % Pt-Al₂O₃ Catalyst

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The isomerization, dehydrocyclization and hydrogenolysis of 2,3-dimethyl[2- 13 C]pentane have been studied at 260°C over a 10 % Pt-Al₂O₃ catalyst of low dispersion, under various hydrocarbon and hydrogen pressures. Most of the isomerization products are accounted for either by a bondshift mechanism or by a cyclic mechanism involving 1,2-dimethylcyclopentane intermediate. The absence of significant scrambling of the label suggests that the rate-determining step in isomerization is the skeletal rearrangement of highly dehydrogenated species. The positive order as a function of hydrogen which is found (0.8-1.2) cannot then be taken as evidence that desorption is rate-determining. It is best explained by assuming multisite adsorption of hydrocarbon and competition with hydrogen for chemisorption on the same sites. The results provide argument in favour of a reactive rather than dissociative-type adsorption step.

The use of ¹³C-labelled molecules has shown that the isomerization of hexanes and pentanes on platinum catalysts takes place according to two basic reaction mechanisms: the cyclic mechanism favoured on highly dispersed catalysts and the bond-shift mechanism on catalysts with large metal particles.¹⁻⁴ By examining the product distributions in methylcyclopentane hydrogenolysis and hexane isomerization, one may further distinguish between a selective cyclic mechanism which occurs on platinum catalysts of low dispersion and interconverts methyl-pentanes but not



selective

non-selective



n-hexane and a non-selective cyclic mechanism on highly dispersed catalysts which provides to an even probability of breaking each cyclic C—C bond in the adsorbed cyclopentane intermediate (fig. 1).^{2, 3, 5}

Finally, classification of the various contact reactions of n-pentane and isopentane on a $Pt-Al_2O_3$ catalyst of low dispersion according to their apparent activation energies allows a distinction to be made between two groups of bond-shift isomerizations.⁶ The first, including methyl shift and isopentane \rightarrow neopentane isomerization, requires the same activation energy as hydrocracking of an internal C—C bond. It is thought that in this case the reaction mechanism involves metallocyclobutane

cyclic mechanism



FIG. 2.—Isomerization of 2,3-dimethylpentane: reaction pathways. ●, actual labelling; □, labelling which could distinguish between different pathways.

and metallocarbene intermediates. A second group, including n-pentane \rightarrow isopentane isomerization and the reverse reaction, requires higher activation energies.

Four reaction mechanisms, two bond-shift and two cyclic, account for isomerization of the C₅-C₆ hydrocarbons. Generalization to higher alkanes requires further investigation. On one hand, complicating the structure of the molecule could make an additional mechanism, not detectable with smaller molecules, possible. On the other hand, steric and electronic effects may also drastically favour a single reaction mechanism.

For these reasons, isomerization on Pt-Al₂O₃ of various heptanes labelled with carbon-13 have been studied and a catalyst of low dispersion was used to make bond-shift reactions observable. 2,3-Dimethylpentane and 2-methylhexane were investigated first because the single dehydrocyclization path in these cases minimizes the number of reaction products and parallel pathways.

In spite of this simplification, because of the number of cyclic and bond-shift rearrangements, all heptane isomers except ethylpentane are expected from 2,3dimethylpentane (2,3-DMP) (fig. 2). Most are formed by different pathways, distinguishable only if the molecule is adequately labelled. 2,3-Dimethyl[2-1³C]pentane was then selected from six possible isotopic varieties because the 3-methylhexanes obtained by cyclic and bond-shift mechanisms are labelled differently and because self-isomerization via adsorbed 1,2-dimethylcyclopentane is easily detectable.

EXPERIMENTAL

ALCOHOLS

Heptanols with various structures labelled with 13 C on carbon 1, on carbon 2 or at the methyl group were prepared by reacting a ketone or an aldehyde with the appropriate alkylmagnesium halide (table 1). Alcohols labelled on carbons 3 and 4 were obtained by reacting an ester, ethyl formate or ethylacetate, with a single Grignard reagent (II-T, IV-X) or a 1/1 mixture of two n-alkyl magnesium bromide (I-T, II-Z), or a 3/1 mixture of isopropyl and ethyl magnesium bromide (III-Y). In the latter cases, two additional symmetrical alcohols of lower and higher molecular weights were obtained; e.g. 2,3,4-trimethyl[3-13 C]pentan-3-ol and 3-methyl[3-13C]pentan-3-ol with 2,3-dimethyl[3-13C]pentan-3-ol (III-Y), [3-13C]pentan-3-ol and [5-13C]nonan-5-ol with [3-13C]heptan-3-ol [II-Z].

The procedure for preparing these compounds in small quantities (\approx 50 mg) with a reasonable yield (60-70 %) has already been described.⁷ The isotopic purity of the starting materials, methyl(13 C) iodide, [1- 13 C] or [2- 13 C]ethyl iodide, sodium formate (13 C), [1- 13 C] ethylacetate and [2-13C] acetone, obtained from Merck, Sharpe and Dohme (Canada) was in some cases ≈ 60 % and others ≈ 90 %.

HYDROCARBONS

All labelled n-heptanes, all 3-methylhexanes except I-U labelled on carbon 4, several labelled 2,3- and all 2,4-dimethylpentanes were prepared from the appropriate labelled alcohols. In a typical experiment, 8-15 mg of alcohol was dehydrated over non-acidic alumina and the resulting olefin hydrogenated at 120° C on 10 % Pt-Al₂O₃ in the same pulse flow system. The temperature of the alumina, 180°C, was such that the extent of skeletal rearrangement and cracking that took place during the dehydration was < 2 %. The impurities resulting from these side reactions were removed by preparative g.l.c., before the labelled hydrocarbons were used for the catalytic experiments or for mass spectrometrical calibrations. The unlabelled 2,3-dimethylpentane was Fluka purum grade (< 0.2 %isomers) and was used without further purification.

CATALYSTS

The 10 % Pt-Al₂O₃ catalyst was prepared by impregnation of a catalytically inert alumina (Woelm A.G.) with chloroplatinic acid and reduction by hydrogen at 200°C for 24 h.

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hydrocarbon R.MgX alcohol q_a q_s		P	PAR	AYI	κE,	AMIR	-EBR	AHI	MI	, e	BAU	ILT A	ANI) FR	ENNET			170 7
hydrocarbonRYCOR'MgXalcohol a_6 a_5 $\uparrow \uparrow \uparrow \downarrow$ I:X3-hexanone $^{13}CH_3$ Mg13-methyll ¹⁻¹⁰ Chexan-3-ol0.0950.93 $\uparrow \uparrow \uparrow \uparrow$ I:Y2-pentanone $(H_3^{-13}CH_3, Mg1)$ 3-methyll ²⁻¹³ Chexan-3-ol0.0950.93 $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ 2-methylbentanal $^{12}CH_3$ Mg13-methyll ²⁻¹³ Chexan-3-ol0.0950.93 $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ 2-methylbentanal $^{12}CH_3$ Mg13-methyll ²⁻¹³ Chexan-3-ol1.000.90 $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \uparrow \uparrow$	a4	0.87	0.92	0.93	0.93	0.10	0.10	0.51	0.51	0.509	0.935	0105	CUL.U	0.855	0.81	0.92	0.505	0.53
hydrocarbonRKCOR'MgXalcohol a_6 $\uparrow \uparrow \uparrow$ I:X3-hexanone 1^3 CH ₃ Mg I3-methyl[1^2C]hexan-3-ol0005 $\uparrow \uparrow \uparrow$ I:Y2-pentanone $(H_3^{-1}^3CH_3 Mg I)$ 3-methyl[1^2C]hexan-3-ol1005 $\uparrow \uparrow \uparrow \uparrow$ I:Y2-pentanone $(H_3^{-1}^3CH_3 Mg I)$ 3-methyl[1^2]c]hexan-3-ol100 $\uparrow \uparrow \uparrow \uparrow$ I:Y2-methylbutanal $^{13}CH_3 Mg I$ 3-methyl[1^{-13}C]hexan-3-ol100 $\uparrow \uparrow \uparrow \uparrow$ I:Y2-methylbutanal $^{13}CH_3 Mg I$ 3-methyl[5^{-13}C]hexan-4-ol0095 $\uparrow \uparrow \uparrow \uparrow \downarrow$ I:W2-methylbutanal $^{13}CH_3 Mg I$ 3-methyl[5^{-13}C]hexan-4-ol0076 $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I:W2-methylbutanal $^{13}CH_3 Mg I$ 3-methyl[5^{-13}C]hexan-4-ol0076 $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow I:WI:W2-methylbutanal^{13}CH_3 Mg I3-methyl[5^{-13}C]hexan-4-ol0076\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow I:WI:W2-methylbutanal^{13}CH_3 Mg I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow \uparrow I:WI:W2-methylbutanal^{13}CH_3 Mg I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow \uparrow I:WI:W2-methylbutanal^{13}CH_3 Mg I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow I:WI:W2-methylbutanal^{13}CH_3 GH I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow I:WI:WI:WI:W^{13}CH_3 Mg I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow I:WI:WI:WI:WI:WI:M^{13}CH_3 GH I^{12}SIChepan-3-ol0076\uparrow \uparrow \uparrow \uparrow I:W$	a ₅	0.93	0.11	0.08	0.95	0.9-0.95	0.94	0.525	0.525	0.98	0.96	6	ол.т	0.935	0.07	0.95	0.56	0.98
hydrocarbonRRCOR'MgXalcohol $\uparrow \uparrow \uparrow \downarrow$ I.X3-hexanone1 ³ CH ₃ Mg I3-methyll ^{1,13} Clhexan-3-ol $\uparrow \uparrow \uparrow \uparrow \downarrow$ I.Z2-methylpentanal1 ³ CH ₃ Mg I3-methyll ^{2,13} Clhexan-3-ol $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.Z2-methylbentanal1 ³ CH ₃ Mg I3-methyll ^{2,13} Clhexan-3-ol $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow I.Y2-methylbentanal13CH3 Mg I3-methyll2,13Clhexan-3-ol\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow I.Y2-methylbutanal13CH3 Mg I3-methyll2,13Clhexan-4ol\uparrow \uparrow \uparrow \uparrow \downarrow I.Y2-methylbutanal13CH3 CH3 Mg I3-methyll2,13Clhexan-4ol\uparrow \uparrow \uparrow \downarrow I.Y2-methylbutanal13CH3 Mg I214Ocheptan-3-ol\uparrow \uparrow \uparrow \downarrow I.Y2-methylbutanal13CH3 Mg I214Ocheptan-3-ol\uparrow \uparrow \downarrow I.Y2-methylbutanal13CH3 Mg B214Ocheptan-3-ol\uparrow \downarrow \downarrow I.Y2-methylbutanal13CH3 Mg B214Ocheptan-3-ol\downarrow \downarrow \downarrow I.Y2-methylbutanal13CH3 Mg B214Ocheptan-3-ol\downarrow \downarrow$	a ₆	0.095	1.00	0.945	1.00	1.00	0.97	0.705	1.00	0.845	0.92	1 00	B	1.00	1.00	0.995	0.755	1.00
hydrocarbonR.Y.COR'MgX $\uparrow \uparrow \uparrow \downarrow$ I.X3-hexanone 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow$ I.Y2-pentanone 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \downarrow$ I.Z2-methylbentanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.Y2-methylbentanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.Y2-methylbentanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.V2-methylbuttanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.V2-methylbuttanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.V2-methylbuttanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I.V2-methylbuttanal 13 CH3, Mg I $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \downarrow$	alcohol	3-methyl[¹³ C]hexan-3-ol	3-methyl[2- ¹³ C]hexan-3-ol	3-methyl[1- ¹³ C]hexan-2-ol	3-methyl[3-13C]hexan-3-ol	3-methyl[5- ¹³ C]hexan-4-ol	3-methyl[6- ¹³ C]hexan-4-ol	[1-13C]heptan-3-ol	[2- ¹³ C]heptan-3-ol	[3- ¹³ C]heptan-3-ol	[4- ^{1,3} C]heptan-4-ol	2 2. dimethyll? _1307nanton_2_01	ליבידיים אינייים אינייים איניים אינ	2,3-dimethyl[3- ¹³ C]pentan-3-ol	2,3-dimethyl[4- ¹³ C]pentan-3-ol	2,4-dimethyl[3- ¹³ C]pentan-3-ol	2,4-dimethyl[1- ¹³ C]pentan-2-ol	2,4-dimethyl[2- ¹³ C]pentan-2-ol
hydrocarbonRR'CO $\uparrow \uparrow \uparrow$ I-X3-hexanone $\uparrow \uparrow \uparrow \uparrow$ I-X3-hexanone $\uparrow \uparrow \uparrow \uparrow$ I-Y2-pentanone $\uparrow \uparrow \uparrow \uparrow$ I-Y2-methylbentanal $\uparrow \uparrow \uparrow \uparrow$ I-Y2-methylbutanal $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I-Y2-methylbutanal $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ I-Y2-methylbutanal $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	R″MgX	¹³ CH ₃ Mg I	CH ₃ - ¹³ CH ₂ Mg I	¹³ CH ₃ Mg I	Et Mg Br+n-Pr Mg Br	CH ₃ ¹³ CH ₂ Mg I	¹³ CH ₃ CH ₂ Mg I	¹³ CH ₃ CH ₂ Mg I	CH ₃ ¹³ CH ₂ Mg I	n-Bu Mg Br + Et Mg Br	n-Pr Mg Br	ç D:: Mc D.	TO BW DO-S	i-Pr Mg Br+Et Mg Br	CH ₃ ¹³ CH ₂ Mg I	i-Pr Mg Br	¹³ CH ₃ Mg I	i-Bu Mg Br
hydrocarbon \downarrow \uparrow	RR/CO	3-hexanone	2-pentanone	2-methylpentanal	CH ₃ ¹³ COOEt	2-methylbutanal	2-methylbutanal	pentanal	pentanal	H13COOEt	H ¹³ COOEt	CH 1300CH	Cu3- CUCu3	CH ₃ ¹³ COOEt	3-methyl-2-butanone	H ¹³ COOEt	4-methyl-2-pentanone	CH ₃ -1 ³ COCH ₃
$ _{\text{hydrocartbol}} $		I-X	I-Y	Z-I	I-T	V-I	M-I	X-11	II-Y	Z-II	11-T	<u>у</u> Ш	V-111	Y-III	z-III	X-VI	Y-VI	IV-Z
	hydrocarboi	×	<	>	$\left\langle \right\rangle$	Ż	\geq	$\left\langle \right\rangle$		$\left\langle \right\rangle$	$\left\langle \right\rangle$	~ -{	/ }	$\left\{ \right.$	4	\downarrow	`-\ •\	$\langle \prec \rangle$

Table 1,—Synthesis and mass spectra of labelled heptanes (a_n values)

Before each run purified hydrogen was passed over the catalyst at 300°C for at least 3 h. Hydrogen chemisorption, oxygen-hydrogen titration ⁸ and X-ray line broadening measurements all gave the same value, 90 Å, for the mean metal crystallite diameter.

APPARATUS AND PROCEDURE

The differential reactor and experimental procedure for catalytic experiments have been described elsewhere.⁹ In each run, a small amount of labelled hydrocarbon (≈ 8 mg) was passed over the catalyst at constant pressure (1.2-20 Torr). Part of the reaction mixture was analysed by chromatography over a DC 200 and a DMS column, part was used for mass spectrometrical location of the label in each molecule using a g.l.c.-m.s. coupling device. Before the g.l.c.-m.s. analysis, the reaction mixture was fractionated twice by preparative gas chromatography : first on DMS to separate cyclic and acyclic C_7 hydrocarbons and then on SE 30 to split acyclic hydrocarbons into three fractions containing (i) 2,2-,2,4- and 3,3dimethylpentanes plus methylcyclopentane, (ii) 2,3-dimethylpentane and (iii) 3-methylhexane and n-heptane.

GAS CHROMATOGRAPHY

Three substrates were used for both analytical (5 m $\times \frac{1}{8}$ in., 5% stationary phase on firebrick) and preparative (5 m $\times \frac{1}{4}$ in., 20 % stationary phase) chromatography. First silicone elastomers SE 30 and DC 200 at 20°C allow separation of all hydrocarbons except 2,3-dimethylpentane and 2-methylhexane. Later these hydrocarbons, with the exception of 2,3-dimethylpentane and 3-methylpexane, are resolved on DMS at 20°C. The 5 m $\times \frac{1}{8}$ in. DC 200 column in the g.l.c.-m.s. device was operated at -15° C with a helium flow rate of 8 cm³ min⁻¹. Under these conditions, 2,3-dimethylbutane and 2-methylpentane, 2,2dimethyl- and 2,4-dimethylpentanes and methylcyclopentane were completely resolved.

MASS SPECTROMETRY

The mass spectrometrical analysis was performed with a CH 7 Varian-Mat apparatus operating with 70 V electrons and a trap current of 300 μ A. The operating conditions for the greatest accuracy during the g.l.c.-m.s. analysis have been described extensively.⁹

The mass spectra were recorded in the parent, -CH₃, -C₂H₅ and -C₃H₇ regions and the treatment of data was basically the same as for the C_5 and C_6 hydrocarbons.^{3, 6} After corrections for naturally occurring isotopes and C-H fragmentation, the mole fractions a_5, a_5 and a_4 of the ions $C_6H_{13}^{\oplus}, C_5H_{11}^{\oplus}$ and $C_4H_9^{\oplus}$ were derived, having retained the carbon-13 during their formation from an isotopically pure labelled hydrocarbon. Carbon-13 in the various molecules was then located by comparing the observed values a_6 , a_5 and a_4 with the a_{6i} , a_{5i} and a_{4i} values of reference hydrocarbons, shown in table 1.

Apart from the general eqn (i)-(iv), where C_i represents the mole fraction of the *i*th isotopic species,

$$\Sigma C_i a_{6i} = a_6 \tag{i}$$

$$\Sigma C_i a_{5i} = a_5 \tag{ii}$$

$$\Sigma C_i a_{4i} = a_4 \tag{iii}$$

$$\Sigma C_i = 1 \tag{iv}$$

more restrictive relationships appropriate to each particular reaction may be used. In the case of n-heptanes, for instance, it was assumed that species II-X was not present in the reaction mixture and therefore only eqn (ii)-(iv) were used. In the case of 2,3-dimethylpentanes, only species III-X and III-Y were thought to be present, so that eqn (iii) and (iv) are sufficient precisely to locate the label in the molecule.

In some cases, the reference hydrocarbons could not be synthesised [2,2-dimethyl- (V) and 3,3-dimethyl-pentanes (VI)] or the compounds yielded were too impure to permit accurate measurement of some or all of the a_n values {3-methyl[4-13C]hexane (I-U) and 2,3-dimethylpentane labelled on the methyl groups}. It was then assumed that the demethylated fragment

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in III and V and the de-ethylated fragment in VI were formed by C—C rupture at a tertiary (III) or quaternary (V, VI) carbon atom and that the a_n values for I-U were the same as for I-V.

RESULTS

PRODUCT DISTRIBUTIONS

The reactions of 2,3-dimethylpentane (2,3-DMP) have been studied at 260°C over a 10 % Pt-Al₂O₃ catalyst under various hydrocarbon and hydrogen pressures (1.2-20 and 200-1150 Torr, respectively). C₇ hydrocarbons represented 80 % of the total reaction products and included *trans*- and *cis*-1,2-dimethyl-cyclopentanes (1,2-DMCP), with an equilibrium ratio 6/1 and six acyclic hydrocarbons : 2,4-dimethylpentane (2,4-DMP), 2-methyl- and 3-methyl-hexanes (2-MH, 3-MH), n-heptane (n-Hep) and 2,2-dimethyl- and 3,3-dimethyl-pentanes (2,2-DMP and 3,3-DMP). Each gemdimethylpentane represented only $\approx 2\%$ of the products. Table 2 shows the distribution of the major C₇ reaction products for various hydrocarbon and hydrogen pressures. By increasing hydrocarbon pressure or decreasing hydrogen pressure, the cyclic products are strongly increased at the expense of 3-MH and n-Hep. Hydrogen but not hydrocarbon pressure also seems to modify the amounts of 2-MH and 2,4-DMP.

TABLE 2.—ISOMERIZATION OF 2,3-DIMETHYLPENTANE. DISTRIBUTION OF C_7 reaction products.

run	P _{HC}	P _{H2}	α _{C7}	2,4-DMP	2-MH	3-MH	n-Hep.	(1,2-DMCP) _t	(1,2-DMCP) _c
1	1.2	760	10.8	9.5	4.8	26.5	27.9	26.9	4.4
2	5	760	8.7	8.2	3.1	26.5	24.3	32.0	5.9
3	10.5	760	9.3	7.2	4.4	24.2	23.1	35.1	5.5
4	20	760	9.0	9.2	3.4	22.0	18.5	40.0	6.9
5	5	200	8.4	3.3	2.4	13.3	10.7	60.2	10.1
6	5	400	11.6	5.7	4.4	21.8	17.5	42.8	7.8
7	5	1150	7.4	9.2	3.6	22.9	24.1	34.5	5.7

Hydrocracking of 2,3-dimethylpentane involves breaking a single carbon-carbon bond and occurs according to one of the following reactions

$$C_7 \to C_6 + C_1 : 53 \pm 4 \%$$
 (15)

$$C_7 \to C_5 + C_2 : 13 \pm 2 \%$$
 (16)

$$C_7 \to C_4 + C_3 : 34 \pm 3 \%.$$
 (17)

De-ethylation (16) and depropylation (17) yield selectively isopentane and n-butane, as expected from a single C—C cleavage. Demethylation (15) provides 2,3-dimethylbutane (22 %), 2-methylpentane (30 %) and 3-methylpentane (42 %) and also methylcyclopentane (6 %).



ISOMERIZATION OF 2,3-DIMETHYL[2-13C]PENTANE

The contact reactions of 2,3[2-¹³C]DMP were studied under the same experimental conditions as in the last section. The label has been located in 3-methylhexane, n-heptane and 2,4-dimethyl- and 2,3-dimethylpentanes.

3-METHYLHEXANES

In all the experiments, a value of unity was found for a_6 , which shows that only four isotopic varieties are present : Y and T, expected by cyclic mechanism :

$$\xrightarrow{} (\underbrace{\downarrow}) \underset{\overline{ADS}}{\longrightarrow} \underbrace{\uparrow}_{1/2} + \underbrace{\uparrow}_{1/2} (1)$$

and U and V, expected by bond-shift:



Since $a_{4u} \equiv a_{4v}$ and $a_{4y} \equiv a_{4t}$, the abundance a_4 of the heavy depropylated fragment allows determination of the sum of the mole fractions u+v and y+t, by solving the equations:

$$a_{4v}(u+v) + a_{4y}(y+t) = a_4$$

 $(u+v) + (y+t) = 1.$

Evaluation of y and t then necessitates the use of a_5 . Since the bases a_{5u} and a_{5v} are not accurately known, in each experiment two values were given for (y, t) corresponding to $a_{5u} = a_{5v} = 0.90$ and $a_{5u} = a_{5v} = 0.95$, respectively (table 3).

The distribution of the 3-MH species are practically independent of hydrocarbon and hydrogen pressures, but y is almost always slightly larger than t, which seems to indicate the minor participation of some process more complicated than the simple cyclic mechanism.

TABLE 3.—ISOMERIZATION TO 3-METHYLHEXANES. DISTRIBUTION OF ISOTOPIC VARIETIES.

	products		\sim					
			ro	\sim	\sim	\frown	\sim	
run no.	P_{HC}	$P_{\rm H2}$	u+v	y ^a	t ^a	y ^b	t ^b	_
1 4	1.2 20	760 760	21 24	37.5 39.5	41.5 36.5	39 41	40 35	
5 2 7	5 5 5	200 760 1150	19 23.5 21	43 38 42	38 38.5 37	44 39.5 43.5	37 37 35.5	

^a Basis $a_{5u} = a_{5v} = 0.90$, ^b Basis $a_5u = a_5v = 0.95$.

n-HEPTANES

A constant value of 0.51 ± 0.01 is found for a_4 , which shows the absence of $[4^{-13}C]n$ -heptane (T). The relative abundance a_5 of the heavy de-ethylated fragment then allows determination of the mole fraction z of $[3^{-13}C]n$ -Hep (Z) and of (x+y), sum of the mole fractions of $[1^{-13}C]$ and $[2^{-13}C]n$ -Heptanes (X and Y). z, although small, is not negligible at low hydrogen and high hydrocarbon pressures (table 4). Since the only isotopic variety expected in a one-step reaction is Y [reaction (2)], it was assumed that x = 0 and a_6 was recalculated accordingly.

$$\xrightarrow{} (\xrightarrow{})_{ADS} \xrightarrow{} ((2)$$

The agreement with the observed values is good (6th column of table 4).

TABLE 4.—n-HEPTANES AND 2,3-DIMETHYLPENTANES. DISTRIBUTIONS OF ISOTOPIC VARIETIES.

	proc	lucts	~~~	or		\leftarrow	\checkmark		
run no.	P _{HC}	P _{H2}	(z)	(<i>x</i> + <i>y</i>)	$\Delta(a_6)$	(x)	(بر)	α _{C7}	y'
1	1.2	760	0	100	+0.025	93.3	6.7	16.1	70
4	20	760	6.5	93.5	-0.015	92.0	8.0	21	60
5	5	200	12	88	-0.015	98.4	1.6	10.2	28
2	5	760	4.5	95.5	+0.01	96.7	3.3	10.9	54
7	5	1150	1	99	-0.005	95.6	4.4	11.9	65
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$$y' = \frac{2y(1-a)}{\alpha} \times 100.$$
 $\Delta a_6 = (a_6) \text{ calc.} - (a_6) \text{ obs}$

2,4-DIMETHYL- AND 2,3-DIMETHYL-PENTANES

In the case of 2,4-dimethylpentane, values of 1.00 and 0.54 were found for a_6 and a_4 in all experiments. Therefore 2,4-dimethylpentane is exclusively labelled on carbon 2, as expected by a one-step bond-shift mechanism

↓ → ↓↓ (10)

In the case of 2,3-dimethylpentane according to reaction (3) only two isotopic species, labelled on carbon 2 (X) and on carbon 3 (Y), are expected :



Indeed, the absence of species labelled on the ethyl or any of the methyl groups is ascertained by the values of unity found for a_6 and a_5 . The relative abundance a_4 of the heavy depropylated fragment allows the determination of y (table 4). The percentage of 2,3-DMP which has been isomerized equals 2y, and only the value $y' = 2y(1-\alpha)100/\alpha$, taking into account conversion α , is comparable with the percentages of isomers in table 2.

For the other molecules obtained by the cyclic mechanism (3-MH and n-Hep), the amounts y' of self-isomerized 2,3-DMP decreased strongly with decreasing hydrogen pressure.

2,2-DIMETHYL- AND 3,3-DIMETHYL-PENTANES

 a_4 was determined for 2,2-DMP in runs 2 and 7 and found equal to 0.90, showing predominant labelling on carbon 2, as expected from a simple methyl shift [reaction (11)]



For 3,3-DMP, a_5 was determined for each run. The values 0.58 ± 0.03 were independent of hydrocarbon and hydrogen pressures and showed that 84% of the label was on carbon 2, methyl shift [reaction (12)] and 16 ± 6 % on carbon 3, ethyl shift [reaction (13)]



CONTRIBUTIONS OF CYCLIC AND BOND-SHIFT MECHANISMS

Using tables 2 to 4, it is possible to calculate the percentages of various molecules obtained according to a bond-shift and a cyclic mechanism and hence to estimate the relative contributions of either mechanism. Such an estimate is made in table 5: the figures reported in column 6, for example, were obtained by multiplying the mole fractions of 3-MH (7th column of table 2) by the percentage (u+v) of 3-MH formed by bond-shift (4th column of table 3) and then normalizing over all the reaction products including 2,3-DMP.

The total percentage of molecules, acyclic or cyclic, formed according to a cyclic mechanism is always large (over 85 %). It increases first with increasing hydrogen pressure from 200 to 760 Torr and then remains practically constant. Simultaneously, a change is observed in the product distribution among each type of isomer: with increasing hydrogen pressure, the ratio 2,4-DMP/2-MH+3-MH increased regularly among the molecules obtained by bond shift and the ratio 3-MH/n-Hep decreased among the cyclic-type isomers (last column of table 5).

				bond	-shift mech	anism						
run no.	$P_{\rm HC}$	P _{H2}	2,4-DMP	2-MH	3-MH	BS %	c.1./m.s.«	2,3-DMP	3-MH	n-Hep	1,2-DMCP	3-MH n-Hep
1	1.2	760	5.6	2.8	3.3	11.7	0.9	41.5	12.2	16.3	18.3	0.75
2	5	760	5.4	2.0	4.0	11.4	0.9	35.7	13.2	15.1	24.6	0.90
4	20	760	5.8	2.2	3.4	11.4	1.05	37.5	10.5	10.9	29.7	0.95
5	5	200	2.6	1.9	2.0	6.5	0.65	22.2	8.5	7.4	55.4	1.15
7	5	1150	5.6	2.2	3.0	10.8	1.1	39.4	10.9	14.5	24.4	0.75

TABLE .	5.—DISTRIBUTION	OF PRODUCTS	CLASSIFIED	ACCORDING	то	REACTION	MECHANISM
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^a Chain lengthening/methyl shift = 2,4-DMP/2-MH+3-MH.

KINETIC DATA

Approximate determinations of the order as a function of hydrocarbon and hydrogen were made as in the case of pentane rearrangements.⁶ Positive orders as a function of hydrogen were found between 0.8 and 1.3 according to the reaction. The order as a function of hydrocarbon was 0.35 ± 0.1 .

DISCUSSION

MAJOR REACTION MECHANISMS

The ¹³C experiments show that most of the C₇ products (over 95 %) may be accounted for by one of the two basic general mechanisms : the predominant cyclic mechanism which involves in this case a 1,2-dimethylcyclopentane intermediate and the bond-shift mechanism corresponding to the displacement of a single C—C bond within the molecule. These two general mechanisms, already demonstrated in the case of C₅ and C₆ hydrocarbons,^{3, 6} may then be extended to hydrocarbons of higher molecular weight.

However, some isotopic species cannot be explained by assuming a single bondshift or cyclic-type reaction. These are $[3^{-13}C]n$ -heptane and part of the 3-methyl $[2^{-13}C]hexane$, since the amount of this molecule exceeds that of $3^{-}MH[3^{-13}C]$ in most experiments. The presence of "abnormal" isotopic species in small amounts (<10 %) is best explained as the result of two consecutive elementary steps in the adsorbed phase.



Such repetitive processes, which have already been observed in hexane isomerization on films or supported catalysts with large metal particles,^{3b} seem to be enhanced by high hydrocarbon and low hydrogen pressures (tables 3 and 4).

Similarly, hydrocracking occurs mainly by simple carbon-carbon bond rupture: n-pentane and isobutane, obtained by consecutive breaking of two carbon-carbon bonds, represent < 2 % of the hydrocracking products and methylcyclopentane, obtained by consecutive ring closure and demethylation, only 3 %. The repetitive processes should therefore be considered minor in hydrogenolysis as in isomerization reactions.

STRUCTURAL EFFECT

Comparison of these results with those obtained on the same catalyst with 2methylpentane and 3-methylpentane¹⁰ demonstrates the structural effects which arise when a methylenic hydrogen is replaced by a methyl group. The contribution of the cyclic mechanism is on the average much higher for isomerization of 2,3-DMP than for the methylpentanes. However, a detailed analysis of the various individual

reactions makes it possible to distinguish between two groups of bond-shift isomerizations: chain lengthening and methyl migration. Fig. 3 represents some reactions interconverting methylpentanes and n-hexane and the homologous reactions with 2,3-DMP. In the chain-lengthening reactions, the contribution of the bondshift mechanism is reduced by a factor of ≈ 1.5 when methylpentanes are replaced by dimethylpentanes. For methyl displacement, reduction of the bond-shift mechanism is more drastic: while bond-shift is predominant in $3-MP \rightarrow 2-MP$ isomerization, it represents only 22 % of the reaction pathways in the homologous reactions of 2,3-DMP.

chain lengthening



FIG. 3.—Parallel between isomerization of methylpentanes and 2,3-dimethylpentane. (1) 2- $MP \rightarrow n$ -hex; values obtained from the amount of 3-MH[2-13C] multiplied by 2 (see table 3). (2) 3-MP \rightarrow 2-MP; values obtained from the relative amounts of 2,4-DMP and 2,3-DMP[2-¹³C] (see table 5).

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This distinction between chain lengthening and methyl migration is the same as that made on the basis of kinetic data in the pentane isomerizations. Obviously, two types of bond-shift reactions do exist, which may be distinguished by their activation energies 6 or by substituent effects (this work).

KINETIC

Although the reaction mechanisms are the same, the kinetic features strongly distinguish the isomerization of 2,3-DMP and that of C_5 and C_6 hydrocarbons carried out under the same experimental conditions. Large negative orders have been found for pentane ⁶ and hexane ¹¹ isomerizations and have been interpreted by the assumption that the rate-determining step was the rearrangement of highly dehydrogenated species. In contrast, the positive order with respect to hydrogen, close to unity, found in the case of 2,3-DMP and the small order with respect to hydrocarbon could signify that the desorption of adsorbed species with high surface concentration is rate-determining.

However, the almost complete absence of repetitive processes, clearly demonstrated by the tracer experiments, shows that surface reactions, *i.e.*, skeletal rearrangements and not product desorption, are rate-determining in the isomerization of 2,3-DMP as in the isomerization of C_5 and C_6 hydrocarbons. One has therefore to interpret with one single kinetic model isomerization reactions which occur with positive and negative orders with respect to hydrogen.

A kinetic model that could account for large variations in order from highly negative to positive values, has been proposed by Frennet *et al.*¹² They assumed that hydrocarbon and hydrogen both compete for chemisorption on the same "potential" sites of the surface: while hydrogen chemisorption requires only one of these sites, a patch of z contiguous free potential sites is required for hydrocarbon adsorption. Applied successfully to the adsorption of methane and ethane on rhodium, Frennet's model could easily be extended to any catalytic reactions on metal.

Applied to skeletal isomerization (Appendix), it could explain both the negative order found for pentane and hexane isomerization and the positive order found for the isomerization of 2,3-DMP, under the same experimental conditions, provided that the fraction of the surface covered by hydrocarbon radicals θ_c is larger in the case of heptanes than for C_5 and C_6 hydrocarbons. Estimation of θ_c requires determination of the hydrocarbon adsorption isotherms in the presence of hydrogen, which is difficult. Some information concerning the values of θ_c for various hydrocarbons may be obtained from the amount of hydrocarbonaceous residues left on the surface after catalytic reaction, as measured by Auger electron spectroscopy. These were found to be much larger when C_7 hydrocarbons rather than C_5 hydrocarbons were reacted on platinum single crystals at 350°C.¹³

The order as a function of hydrogen in the case of non-negligible hydrocarbon adsorption always includes both the number m of hydrogen atoms removed to form the reactive species and the number z of metal atoms involved in hydrocarbon adsorption. Differences between the values of m or z or both associated with the different reaction mechanisms could then account for the change with hydrogen pressure in the percentages of molecules formed according to the two bond-shift and the cyclic mechanisms (table 5).

Among the molecules formed by a cyclic mechanism, the enhancement of the dehydrocyclization products with decreasing hydrogen pressure is a further proof that the dehydrogenation steps leading to reactive species are all equilibrated and that skeletal rearrangement is rate-determining. According to the cyclic mechanism,

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	HYDROCARBON ISO	MERIZATION ON	Pt-Al ₂ O ₃
	$\left\{ \frac{m-2 \text{ steps (III)}}{m \text{ steps}} \right\}$	$\int m-2 \operatorname{steps}_{(\mathrm{TTL})}$	$\begin{cases} 1 & (111) \\ m \text{ steps } (1V') \end{cases}$
hydrogenation	of cyclopentane adsorbed species $C-(C_nH_{x)a} + H_a \rightleftharpoons C-(C_nH_{x+1})a + S$ $C-(C_nH_{2n-1})a + H_a \rightleftharpoons (C_nH_{2n}) + z'S$ of acyclic adsorbed isomers $I-(C_nH_{x)a} + H_a \rightleftharpoons I-(C_nH_{x+1})a + S$ $I-(C_nH_{2n})a + H_a \rightleftharpoons I-(C_nH_{2n+1})a + S$ $I-(C_nH_{2n+1})a + H_a \rightleftharpoons I-(C_nH_{2n+2}) + zS$	or $\mathrm{C} ext{-}(\mathrm{C}_{n}\mathrm{H}_{x})_{a}+\mathrm{S}+\mathrm{H}_{2}\rightleftharpoons\mathrm{C} ext{-}(\mathrm{C}_{n}\mathrm{H}_{x+1})_{a}+\mathrm{H}_{a}$ $\mathrm{C} ext{-}(\mathrm{C}_{n}\mathrm{H}_{x-1})_{a}+\mathrm{H}_{a}$	$C-(C_{n}H_{2n-1})_{a}+H_{2} \rightleftharpoons C-(C_{n}H_{2n})+H_{a}+z'S$ $I-(C_{n}H_{n})_{a}+S+H_{2} \rightleftharpoons I-(C_{n}H_{n+1})_{a}+H_{a}$ $I-(C_{n}H_{2n+1})_{a}+S+H_{2} \rightleftharpoons I-(C_{n}H_{2n+1})_{a}+H_{a}$ $I-(C_{n}H_{2n+1})_{a}+H_{2} \rightleftharpoons I-(C_{n}H_{2n+2})+H_{a}+zS$
<u> </u>		(<i>c</i>) (<i>b</i>)	
skeletal rearrangement (a) rate-determining ster	$\left\{ (J) \underset{scheme^{-1.4}}{\text{unimolecular}} \right\}$	$(\mathbf{C}_n\mathbf{H}_x)_a \rightarrow \mathbf{C}\cdot(\mathbf{C}_n\mathbf{H}_x)_1$ $\mathbf{C}\cdot(\mathbf{C}_n\mathbf{H}_x)_1 \rightleftharpoons \mathbf{C}\cdot(\mathbf{C}_n\mathbf{H}_x)_2$ $\mathbf{C}\cdot(\mathbf{C}_n\mathbf{H}_x)_2 \rightleftharpoons \mathbf{J}\cdot(\mathbf{C}_n\mathbf{H}_x)_a$	$\left\{ \begin{array}{ll} \text{(II)} & \text{bimolecular} \\ \text{scheme}^{12} \end{array} \right.$
dehydrogenation (<i>m</i> equilibrated steps)	$\begin{split} \mathbf{C}_{n}\mathbf{H}_{2^{n+2}}+\mathbf{z}\mathbf{S} &\rightleftharpoons (\mathbf{C}_{n}\mathbf{H}_{2^{n+1}})_{a}+\mathbf{H}_{a}\\ \mathbf{(C}_{n}\mathbf{H}_{2^{n}})_{a}+\mathbf{S} &\rightleftharpoons (\mathbf{C}_{n}\mathbf{H}_{2^{n-1}})_{a}+\mathbf{H}_{a}\\ \mathbf{(C}_{n}\mathbf{H}_{z+1})_{a}+\mathbf{S} &\rightleftharpoons (\mathbf{C}_{n}\mathbf{H}_{z})_{a}+\mathbf{H}_{a} \end{split}$	ъ	$\begin{split} \mathbf{C}_{n}\mathbf{H}_{2n+2} + \mathbf{zS} + \mathbf{H}_{a} & \approx (\mathbf{C}_{n}\mathbf{H}_{2n+1})_{a} + \mathbf{H}_{2} \\ \mathbf{(C}_{n}\mathbf{H}_{2n+1})_{b} + \mathbf{H}_{a} & \approx (\mathbf{C}_{n}\mathbf{H}_{2n})_{a} + \mathbf{H}_{2} + \mathbf{S} \\ \mathbf{(C}_{n}\mathbf{H}_{x+1})_{a} + \mathbf{H}_{a} & \approx (\mathbf{C}_{n}\mathbf{H}_{x})_{a} + \mathbf{H}_{2} + \mathbf{S} \end{split}$

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FIG. 4.--Elementary steps in cyclic mechanism.

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the skeletal rearrangement may be decomposed in several consecutive steps: (a) ring closure to form a cyclopentane intermediate $C-(C_nH_x)_1$, (b) fast interconversion between various cyclopentane species and (c) the reopening of one of these species $C-(C_nH_x)_2$ to form an acyclic adsorbed molecule $I-(C_nH_x)_a$ with isomeric structure (fig. 4).

By using one of the reaction schemes developed in Appendix 1, the ratio ρ between the amounts of acyclic and cyclic molecules is expressed as

$$\rho = \mathbb{K} p_{\mathrm{H}} \theta_{\mathrm{S}}^{z'-z} \quad (\text{see Appendix 2}) \tag{v}$$

where z' and z represent the number of potential sites required for the adsorption of a cyclic and an acyclic molecule, respectively. Were z' and z identical, eqn (v) would provide a straightforward explanation of the increase in the percentage of cyclic molecules with decreasing hydrogen pressure. However, the smaller but definite increase in the percentage of cyclic molecules with increasing hydrocarbon pressure suggests different values for z and z', with z' larger than z since θ_s may be expressed as $p_{\rm H}^{\rm a}/p_{\rm HC}^{\rm b}$.¹² Both terms in $\theta_{\rm S}$ and $p_{\rm H}$ in eqn (v) then contribute to the variation of ρ with hydrogen pressure, the latter being predominant.

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APPENDIX 1

SIGNIFICANCE OF ORDER IN SKELETAL ISOMERIZATION OF HYDROCARBON ON METAL

The number of "potential sites" involved in the chemisorption of light alkanes may be as large as 8 (CH₄ on Rh; 12 C₂H₆ on Rh¹⁶). The adsorption rate of the hydrocarbon is then written

$$R_a = k_1 p_{\rm HC} \theta_{\rm H} \theta_{\rm S}^z \tag{A1}$$

for a reactive adsorption step: $HC + H_a + zS \rightarrow$

 $R_a = k_1 p_{\rm HC} \theta_{\rm S}^z$ (A2)

for a dissociative adsorption step : $HC + zS \rightarrow$, where S represents a free potential site, $\theta_{\rm H}$ and $\theta_{\rm s}$, respectively, the fraction of sites covered by hydrogen and the fraction of free potential sites, $p_{\rm HC}$ the hydrocarbon partial pressure, k_1 the rate constant of the adsorption step. Supposing that the fraction of the metal surface not covered by hydrocarbon radicals behaves like a bare surface towards hydrogen chemisorption ¹⁵

$$\theta_{\rm H} = \theta_{\rm H}^{\circ} (1 - \theta_{\rm C}) \tag{A3}$$

then

or

$$\theta_{\rm S} = 1 - \theta_{\rm H} - \theta_{\rm C} = (1 - \theta_{\rm H}^{\circ})(1 - \theta_{\rm C}) \tag{A4}$$

where $\theta_{\mathbf{H}}^{\circ}$ represents the hydrogen coverage in absence of chemisorbed hydrocarbon radicals. Eqn (A1) and (A2) are then written

$$R_a = k_1 p_{\rm HC} \theta_{\rm H}^{\circ} (1 - \theta_{\rm H}^{\circ})^z (1 - \theta_{\rm C})^{z+1} \tag{A5}$$

and

$$R_a = k_1 p_{\rm HC} (1 - \theta_{\rm H}^{\circ})^z (1 - \theta_{\rm C})^z. \tag{A6}$$

It has been shown ¹² that the function $(1-\theta_{\rm H}^{\circ})^{z}$ represents an important inhibiting term in hydrogen pressure. As the value of z may be as large as 8, the function

 $(1-\theta_c)^z$ or $(1-\theta_c)^{z+1}$ needs to be considered even for small values of θ_c , in the range of a few percent.

In the general expression

$$\theta_{\rm C} = K_{\rm C} p_{\rm HC} / p_{\rm H}^{\delta} \tag{A7}$$

 $\theta_{\rm C}$ depends mainly, at a given temperature and partial pressure of hydrogen and hydrocarbon, upon the relative heat of adsorption of hydrogen and hydrocarbon and through δ upon the degree of dehydrogenation of the most abundant surface hydrocarbon radical. For values of z near 7 for methane or near 8-9 for ethane, the functions $p_{\rm HC}(1-\theta_{\rm C})^z$ and $p_{\rm HC}(1-\theta_{\rm C})^{z+1}$ go through a maximum in the region of 10-15 % θ_c . This means ¹² that the hydrocarbon pressure dependence associated with these functions goes from +1 to 0 when θ_c goes from 0 to 0.10 to 0.15 and becomes negative for θ_c values >0.10-0.15. Simultaneously, according to the value of δ , functions $(1-\theta_c)^z$ and $(1-\theta_c)^{z+1}$ have a more or less positive dependence on H_2 pressure which, in the 10 to 15 % θ_c range, may take values larger than the negative dependence contained in the $(1 - \theta_{\rm H}^{\circ})^z$ function.

Thus, even when the rate-determining step is the adsorption, important variations in the order as a function of hydrogen and hydrocarbon may be expected when θ_{c} is altered by changing the hydrogen partial pressure ¹² or by modifying the structure of the reacting hydrocarbon, changing $K_{\rm C}$ and/or δ in eqn (A7).

However, in isomerization of 2,3-dimethylpentane, the labelling experiments showed that skeletal rearrangement and not adsorption was the rate-determining step. It is therefore interesting to analyse the rate equation in this case.

Assume that the dehydrogenated species which isomerize are formed by mconsecutive equivalent dehydrogenation steps, all equilibrated and that the model discussed above for the adsorption step applies. Call K_i the equilibrium constant for the *i*th dehydrogenation step and k the rate constant for the surface skeletal rearrangement. Both the adsorption and surface dehydrogenation steps may be of the reactive or dissociative type.

Reactive adsorption step is

$$C_n H_{2n+2} + H_a + zS \rightleftharpoons (C_n H_{2n+1})_a + H_2.$$
(A8)

Dissociative adsorption step is

$$C_n H_{2n+2} + zS \rightleftharpoons (C_n H_{2n+1})_a + H_a.$$
(A9)

Reactive surface dehydrogenation step is

$$(\mathbf{C}_{n}\mathbf{H}_{x+1})_{a} + \mathbf{H}_{a} \rightleftharpoons (\mathbf{C}_{n}\mathbf{H}_{x})_{a} + \mathbf{H}_{2}$$
(A10)

as an alternative, the site occupied by H_a is liberated

$$(C_n H_{x+1})_a + H_a \rightleftharpoons (C_n H_x)_a + S + H_2.$$
(A11)

Dissociative surface dehydrogenation step is

$$C_n H_{x+1})_a \rightleftharpoons (C_n H_x)_a + H_a \tag{A12}$$

as an alternative, the H_a atom needs one site

$$(C_n H_{x+1})_a + S \rightleftharpoons (C_n H_x)_a + H_a.$$
(A13)

The corresponding concentrations in the surface hydrocarbon radicals formed are

$$\theta_{C_n H_{2n+1}} = K_i \theta_H \theta_S^z \frac{p_{HC}}{p_H}$$
(A14)

$$\theta_{C_n H_{2n+1}} = K_i \theta_S^z \, \frac{p_{\rm HC}}{\theta_{\rm H}} \tag{A15}$$

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$$\theta_{C_n H_x} = K_i \theta_{C_n H_{x+1}} \frac{\theta_H}{p_H}$$
(A16)

$$\theta_{C_n H_x} = K_i \theta_{C_n H_{x+1}} \frac{\theta_H}{\theta_S p_H}$$
(A17)

$$\theta_{C_n H_x} = K_i \theta_{C_n H_{x+1}} \frac{1}{\theta_H}$$
(A18)

$$\theta_{C_n H_x} = K_i \theta_{C_n H_{x+1}} \frac{\theta_s}{\theta_H}.$$
 (A19)

The overall reaction rate may be expressed by combining the various possibilities for the adsorption and surface dehydrogenation steps. As a reactive adsorption mechanism is the most probable one for methane and ethane on rhodium, the association of such an adsorption step with the four possibilities considered here for the dehydrogenation step are analysed. Only dissociative dehydrogenation steps are combined with a dissociative adsorption.

Reactive adsorption followed by m surface reactive dehydrogenation steps of type (10)

$$v = k \prod_{i}^{m} K_{i} \frac{\theta_{\rm H}^{(m+1)}}{p_{\rm H}^{(m+1)}} \theta_{\rm S}^{z} p_{\rm HC}.$$
 (A20)

Reactive adsorption followed by m surface reactive dehydrogenation steps of type (11)

$$v = k \prod_{\substack{i=1\\ H}}^{m} K_{i} \frac{\theta_{H}^{(m+1)}}{p_{H}^{(m+1)}} \theta_{S}^{(z-m)} p_{HC}.$$
 (A21)

Reactive adsorption followed by m surface dissociative dehydrogenation steps of type (12)

$$v = k \prod_{i}^{m} K_{i} \frac{1}{p_{\rm H} \theta_{\rm H}^{(m-1)}} \theta_{\rm S}^{z} p_{\rm HC}.$$
 (A22)

Reactive adsorption followed by m surface dissociative dehydrogenation steps of type (13)

$$v = k \prod_{i}^{m} K_{i} \frac{1}{p_{\rm H} \theta_{\rm H}^{(m-1)}} \theta_{\rm S}^{(z+m)} p_{\rm HC}.$$
 (A23)

Dissociative adsorption followed by m surface dissociative dehydrogenation steps of type (12)

$$v = k \prod_{i}^{m} K_{i} \frac{1}{\theta_{\mathrm{H}}^{(m+1)}} \theta_{\mathrm{S}}^{z} p_{\mathrm{HC}}.$$
 (A24)

Dissociative adsorption followed by m surface dissociative dehydrogenation steps of type (13)

$$v = k \prod_{i}^{m} K_{i} \frac{1}{\theta_{\rm H}^{(m+1)}} \theta_{\rm S}^{(z+m)} p_{\rm HC}.$$
 (A25)

Introducing the dependence of θ_s on θ_H and θ_C in these equations these six cases, respectively, become

(A20)
$$\rightarrow v = k \prod_{i}^{m} K_{i} \frac{\theta_{\rm H}^{\circ (m+1)} (1 - \theta_{\rm H}^{\circ})^{z}}{p_{\rm H}^{(m+1)}} (1 - \theta_{\rm C})^{(m+z+1)} p_{\rm HC}$$
 (A26)

(A21)
$$\rightarrow v = k \prod_{i}^{m} K_{i} \frac{\theta_{\rm H}^{\circ(m+1)} (1-\theta_{\rm H}^{\circ})^{(z-m)}}{p_{\rm H}^{(m+1)}} (1-\theta_{\rm C})^{(z+1)} p_{\rm HC}$$
 (A27)

(A22)
$$\rightarrow v = k \prod_{i}^{m} K_{i} \frac{(1-\theta_{\rm H}^{\circ})^{z}}{p_{\rm H} \theta_{\rm H}^{\circ (m-1)}} (1-\theta_{\rm C})^{(z-m+1)} p_{\rm HC}$$
 (A28)

(A23)
$$\rightarrow v = k \prod_{i}^{m} K_{i} \frac{(1 - \theta_{\rm H}^{\circ)^{z+m}}}{\theta_{\rm H}^{\circ(m-1)} p_{\rm H}} (1 - \theta_{\rm C})^{(z+1)} p_{\rm HC}$$
 (A29)

(A24)
$$\rightarrow v = k \prod_{i}^{m} K_{i} \frac{(1 - \theta_{\rm H}^{\circ})^{z}}{\theta_{\rm H}^{\circ(m+1)}} (1 - \theta_{\rm C})^{(z-m-1)} p_{\rm HC}$$
 (A30)

$$(A25) \to v = k \prod_{i}^{m} K_{i} \frac{(1 - \theta_{\rm H}^{\circ)^{z+m}}}{\theta_{\rm H}^{\circ(m+1)}} (1 - \theta_{\rm C})^{(z-1)} p_{\rm HC}.$$
(A31)

All rate eqn (A26) to (A31) include two terms: one, $g(\theta_{\rm H}^{\circ}, p_{\rm H})$ independent of hydrocarbon coverage, is associated with a formal negative order as a function of hydrogen. The other, $f(\theta_{\rm C})$, is a function of $\theta_{\rm C}$ and for large values of δ in eqn (A7) has an important positive dependence on hydrogen pressure. One may expect that when $\theta_{\rm C}$ goes from small values ($\theta_{\rm C} < 0.01$) to medium values of 0.1-0.2, the order for the hydrocarbon pressure decreases from +1 to 0 and even becomes negative, and simultaneously the order for the H₂ pressure goes from very negative to positive values.

Furthermore, note that if values of z are large enough (z > 8), for half of the above equations the functions of $1 - \theta_c$ are close and similar to those included in eqn (A5) and (A6) obtained on the assumption that adsorption is rate-determining. On the other hand, the function $g(\theta_{H}^{\circ}, p_{H})$ may be considered to be the product of the corresponding g functions, $\theta_{H}^{\circ}(1-\theta_{H}^{\circ})^{z}$ or $(1-\theta_{H}^{\circ})^{z}$ in eqn (A5) and (A6) by an inhibiting factor. This factor in eqn (A26) and (A27) includes a hydrogen partial pressure with a high negative exponent (-m-1). Therefore an important negative hydrogen pressure dependence results from $g(\theta_{H}^{\circ}, p_{H})$ and becomes more important as the active hydrocarbon radical is more dehydrogenated. In eqn (A28) and (A29), the inhibiting term only includes p_{H}^{-1} and is much less efficient. Lastly, in eqn (A30) and (A31), the inhibiting factor is a function of θ_{H}° only and is thus related to the thermodynamics of hydrogen adsorption.

The high negative orders obtained when θ_c is small enough are related to the function $g(\theta_H^\circ p_H)$ and to the inhibiting factor. These allow classification of the six schemes considered according to the importance of the total inhibiting effect of H₂ pressure, in the following sequence:

$$26 > 27 \simeq 29 > 28 \simeq 31 > 30.$$

Remember that, in this sequence, only eqn (A26) and to a lesser extent (A27) and (A29) are significantly different by their g function from eqn (A5) and (A6) in corresponding to an adsorption rate-determining step.

Similarly, the positive orders observed in the case of moderate hydrocarbon coverage are related to the function $f(\theta_c)$. Here again eqn (A26) differs significantly from eqn (A27) to (A31) and also from eqn (A5) and (A6). Among all the possible reaction schemes then, three, eqn (A26) and to a lesser extent eqn (A27) and (A29), give good account for the large difference in orders observed in skeletal rearrangement : from -3.6 in isomerization of n-pentane to +1.2 and +1.8 in isomerization of 2,3-dimethylpentane and 2-methylhexane,¹⁷ respectively. All three equations correspond to a reactive-type adsorption step and it is worth recalling that in some cases ^{12, 16} experimental evidence has been provided in favour of a reactive adsorption step.

On the other hand, no rigid demands have yet been introduced for the surface limiting step. If the surface rate limiting step is characterized by conditions concerning the number of potential sites involved, it may appear as $\theta_{\rm x}^{\rm g}$ in the overall rate equation. The functions $(1-\theta_{\rm H}^{\circ})$ and $(1-\theta_{\rm C})$ in eqn (A26) to (A31) will then be affected by an exponent greater by +z. The fact that the relative contributions of the two bond-shift and the cyclic mechanisms are modified by changing the hydrogen pressure has been interpreted by assuming that the reactive species differ by the number m of dehydrogenation steps.⁶ It could also be an indication that the number z of potential sites involved during the rate-determining step differs in the bond-shift from the cyclic mechanism. This might be related to the number of carbon atoms in the hydrocarbon radical that are bound to the surface, or to the area necessary because of steric interactions to form a cyclic or bond-shift intermediate.

In conclusion,

(1) So many possibilities arise from this analysis that one needs at least some idea of the extent of the coverage and its dependence on partial pressure to distinguish which of the considered schemes are most probable.

(2) However the order as a function of hydrogen cannot be taken as an evidence of the nature of the rate-determining step.

(3) Any change in hydrocarbon coverage, even if it be slight, which may result from an alteration in the structure of the reacting hydrocarbon is expected to induce drastic changes in the order as a function of hydrogen, e.g., from negative to positive.

(4) The latter conclusion, which has already arisen in the case of an adsorption rate-determining step, applies more strongly in the case of a surface rate-determining step.

APPENDIX 2

In fig. 4 are represented two possible reaction schemes for cyclic-type isomerization, which apply according to whether the dehydrogenation steps are dissociative [scheme (I)] or reactive [scheme (II)]. Both the cyclic and acyclic isomeric species are linked to the cyclic and acyclic products by a succession of hydrogenation steps which are all equilibrated and are formally the reverse of the dehydrogenation steps. Call K_i' and K_i the equilibrium constants for reactions (III, III') and (IV, IV') and call z' and z the number of sites required for adsorption, respectively. In the case of unimolecular dissociative adsorption [reactions (III) and (IV)]:

$$\frac{\left[\mathbf{C}-(\mathbf{C}_{n}\mathbf{H}_{2n})\right]}{\left[\mathbf{C}-(\mathbf{C}_{n}\mathbf{H}_{2n})_{a}\right]} = \prod_{i}^{m-2} K_{i}'\left(\frac{\theta_{\mathrm{H}}}{\theta_{\mathrm{S}}}\right)^{m-2} \theta_{\mathrm{S}}^{-z'+1}, \qquad \frac{\left[\mathbf{I}-(\mathbf{C}_{n}\mathbf{H}_{2n+2})\right]}{\left[\mathbf{I}-(\mathbf{C}_{n}\mathbf{H}_{x})_{a}\right]} = \prod_{i}^{m} K_{i}\left(\frac{\theta_{\mathrm{H}}}{\theta_{\mathrm{S}}}\right)^{\Xi} \theta_{\mathrm{S}}^{-z+1}$$

and, in the case of bimolecular reactive adsorption [reactions (III') and (IV')]:

$$\frac{\left[\underline{C}\cdot(\underline{C}_{n}\underline{H}_{2n}^{\mathfrak{f}})\right]}{\left[\underline{C}\cdot(\underline{C}_{n}\underline{H}_{x})_{a}\right]} = \prod_{i}^{m-2} K_{i}^{\prime}\left(\frac{\theta_{S}}{\theta_{H}}\right)^{m-2} p_{H}^{m-2} \theta_{S}^{-z^{\prime}-1}, \quad \frac{\left[\underline{I}\cdot(\underline{C}_{n}\underline{H}_{2n+2})\right]}{\left[\underline{I}\cdot(\underline{C}_{n}\underline{H}_{x})_{a}\right]} = \prod_{i}^{\lceil m \rceil} K_{i}\left(\frac{\theta_{S}}{\theta_{H}}\right)^{m} p_{H}^{m} \theta_{S}^{-z^{-1}}.$$

However, although reaction (c), unlike reaction (b), is not equilibrated, since the reverse reaction like (a) is the slowest step in the whole process, one may consider in a steady state regime the concentration of the acyclic species $[I-(C_nH_x)_a]$ to be proportional to the concentration of the cyclic precursor $[C-(C_nH_x)_a]$:

$$[\operatorname{I-}(\operatorname{C}_n\operatorname{H}_x)_a]/[\operatorname{C-}(\operatorname{C}_n\operatorname{H}_x)_a] = K''.$$

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The ratio ρ between the amounts of acyclic and cyclic products is equal in the case of dissociative adsorption to

$$\rho = \frac{\left[I - (C_n H_{2n+2})\right]}{\left[C - (C_n H_{2n})\right]} = \frac{\prod_i^m K_i}{\prod_i^{m-2} K_i'} K'' \left(\frac{\theta_H}{\theta_S}\right)^2 \theta_S^{z'-z} = \mathbf{K} p_H \theta_S^{z'-z}$$
(V)

and the same value is found for reactive adsorption.

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