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The Isomerization of Aliphatic Hydrocarbons over Evaporated Films of Platinum and Palladium

J. R. ANDERSON* AND N. R. AVERY†

From the Chemistry Department, University of Melbourne, Australia

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Saturated hydrocarbons in the presence of excess hydrogen undergo catalytic skeletal isomerization and hydrocracking at a platinum surface. For mechanistic purposes, a study has been made of these reactions (i) with ethane, *n*-butane, isobutane, neopentane, and isopentane over unoriented evaporated films of platinum and palladium, (ii) with *n*-butane and isobutane over (111) and (100) oriented films of platinum, and (iii) with *n*-butane-1-C^{13} over unoriented films of platinum. Platinum films exposing (111) and (100) surfaces were prepared by deposition on mica and on an evaporated sodium chloride layer, respectively.

Over palladium, most of the reaction was hydrocracking: In no case did isomerization contribute more than about 3% to the initial reaction products. Over platinum, the proportion of isomerization product was substantial. Isobutane isomerized more readily than *n*-butane and the isomerization of the former, but not of the latter, was markedly increased by using a (111) platinum surface. Reactions with both *n*- and isobutane over (100) platinum gave product distributions only marginally different from unoriented platinum.

The main features of the distributions of hydrocracking products could be approximately accounted for by assuming that the residence of a molecule on the surface resulted in the rupture of not more than one carbon–carbon bond. Initial product distributions were substantially independent of temperature. With reaction mixtures having $p_{H_2}/p_{HC} < 1$, there was evidence for the incorporation of carbon into the palladium, but this did not occur with platinum. On both metals, ethane was much less reactive than were the other hydrocarbons, which were all of comparable reactivity. This was reflected in the activation energy, which was much higher for ethane than for the other hydrocarbons. The dependence of reaction rate on pressure indicated that the butanes were, relative to hydrogen, adsorbed much more strongly on palladium than on platinum. On the other hand, ethane was adsorbed equally strongly on both metals.

The isobutane formed from *n*-butane-1-C^{13} was labeled only in the 2-position (i.e., peripherally). No scrambling of the C^{13} occurred. The isomerization was thus entirely intramolecular. At the same time *n*-butane-2-C^{13} was produced in a constant proportion to the isobutane. These products were thus probably formed concurrently from a common surface intermediate.

From arguments based on the influence of hydrocarbon geometry on the reaction, it was concluded that the surface intermediate for isomerization and hydrocracking was 1–3 diadsorbed, except in the case of ethane which was 1–2 diadsorbed. In agreement with this, a 1–3 diadsorbed intermediate provided a reasonably satisfactory quantitative account of the proportion of *n*-butane-2-C^{13} relative to isobutane in the reaction products. The exceptionally high degree of isomerization of isobutane on (111) platinum was tentatively ascribed to a symmetrical triadsorbed surface intermediate.

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* Present address: School of Physical Sciences, Flinders University, Bedford Park, Adelaide, Sout Australia.

† Present address: School of Chemical Sciences, University of East Anglia, Norwich, England.

INTRODUCTION

The skeletal isomerization of saturated hydrocarbons over dual-function catalysts of the platinum/alumina-silica type has been known and studied for some years [e.g., Mills *et al.* (*1*), Sinfelt *et al.* (*2*)]. However, it has recently been shown by Anderson and Baker (*3*) and by Anderson and Avery (*4*), that skeletal isomerization also occurs on evaporated films of platinum, in which the metal is the sole seat of catalytic activity. This conclusion has also been recently confirmed by the work of Gault *et al.* (*5*). The purpose of the present paper is to describe work which was designed to elucidate the mechanism of this reaction.

We have approached the problem in three main ways. The first has been to study the influence of hydrocarbon geometry on the reaction and for this purpose we have compared the reactions of *n*-butane, isobutane, and neopentane. The second has been the use of a surface of known crystallographic orientation so as to define more clearly the geometry of the adsorbed reaction intermediates. The third has been the use of reactant labeled with C^{13} and here the information sought has been the distribution and position of C^{13} atoms in the reaction products.

EXPERIMENTAL

The apparatus and technique, and the details for the preparation of unoriented metal films were generally the same as described by Anderson and Baker (*3*). Film weights for unoriented films were in the range 6–15 mg and were used with a standard size reaction vessel to expose an effective surface area of platinum in the reaction of 400 cm^2, independent of film weight [cf. Anderson and Baker (*3*)]. Attempts to measure the surface areas of used (unoriented) palladium films by means of xenon adsorption at 90°K gave highly irreproducible behavior, with results for various films lying in the range 320–6000 cm^2. This is believed due to a physical breakdown of the film as the absorbed hydrogen escapes during pumping and cooling prior to xenon adsorption. Some visual evidence for physical breakdown was also apparent. It has therefore been assumed that the effective film area for palladium in the reaction was the same as for platinum.

The standard reaction mixture contained 3.7 torr of hydrocarbon and 44.5 torr of hydrogen, measured with the reaction vessel at 0°C; with a standard size reaction vessel, 1 torr is equivalent to 2.02×10^{19} molecules in the reaction volume.

Oriented Films

Oriented films of platinum were prepared by deposition (a) onto a sheet of mica, or (b) on top of an evaporated layer of sodium chloride, as devised by Baker (*6*). Methods (a) and (b) give orientations with the (111) and (100) planes, respectively, parallel to the substrate. For method (a), the freshly cleaved mica sheet (11 × 20 cm) was rolled up and inserted through the neck of a standard size reaction vessel. On unrolling inside, the mica sheet expanded against the walls, thus covering the entire parallel-sided region of the vessel. To facilitate insertion of the mica roll, the reaction vessel carried a B-34 socket instead of the B-24 cone which was otherwise used. With the mica sheet in place, the only region where there was a significant area of metal deposited onto glass was the hemispherical base of the reaction vessel: The area of the latter amounted to about 75 cm^2 compared with about 220 cm^2 on the mica. After the normal baking and outgassing procedure, platinum was deposited in vacuum with the entire vessel maintained at about 400°C. About 20 mg of platinum was evaporated in about 20 min. For method (b), the reaction vessel contained two evaporation filaments. One, for platinum evaporation, was the same as used in other experiments except for being about 30% longer and bent into an open double spiral. This was done to minimize shaddowing due to the presence of the second filament. The second filament was a narrow hairpin situated adjacent to the spiral filament and was bent from a twisted double strand of 0.3-mm diameter tantalum wire. This tantalum filament was coated with about 100 mg of sodium chloride by dipping it into the molten salt. Electron microscopic examination of surface replicas (*vide infra*) showed that about 100 mg of sodium chloride evaporated in about 4 min gave the smoothest surface; less than this gave a generally rougher surface due to small asperities, while more than this tended to produce stepped features after the style of the Babylonian Ziggurat.

The normal outgassing time for the platinum evaporator was about 17 hr, but it was found that over this extended period, radiant heating of the tantalum filament caused considerable evaporation of sodium chloride. Therefore, the following outgassing technique was adopted: The reaction vessel was baked and the platinum evaporator was outgassed in the normal way but without the tantalum filament in place. After cooling and admitting dry air to the system, the reaction vessel was removed and the tantalum filament mounted as quickly as possible. The reaction vessel was then rebaked for 17 hr at 380°C and the platinum evaporator re-outgassed for 30 min. With the reaction vessel at 350°C but with no current through the platinum evaporator, the sodium chloride was then evaporated by passing 3.7 amp through the tantalum filament for about 4 min. After the evaporation of the sodium chloride, the temperature of the reaction vessel was adjusted to 400°C and about 20 mg of platinum were evaporated in about 20 min. In order to increase the thickness of the platinum films produced in this way, the normal reaction vessel was replaced by one of 48-mm diameter and this was estimated to increase the platinum thickness by a factor of about 2 compared with the normal reaction vessel. With this smaller reaction vessel, 1 torr is equivalent to 1.06×10^{19} molecules in the reaction volume. The reduced diameter of the vessel also helped to minimize shadowing due to the presence of the second filament. The vacuum under which the films were deposited by methods (a) and (b) was not significantly different from that obtaining in the deposition of an unoriented film with the vessel at 0°C [cf. Anderson and Baker (*3*)].

After use, the platinum film was stripped from the substrate using 10% aqueous hydrofluoric acid for films on mica, and water for films on sodium chloride. These were then examined by transmission electron microscopy and electron diffraction in a Seimens Elmiskop 1 at 100 kV. In some representative cases the topography of the metal surface was checked by replication. To do this, carbon/platinum was evaporated at 20° incident angle onto the surface of the platinum film which was still adhering to the substrate. The entire duplex film was then stripped from the substrate and the original platinum film was removed from the replica by treatment with aqua regia. Some of the platinum in the replica was probably also removed during this process, but there remained ample contrast in the resultant micrograph.

The effective surface area of platinum films on the mica substrate has been taken as 400 cm^2, independent of film weight, while for a sodium chloride substrate in the smaller vessel, the corresponding figure is taken as 200 cm^2.

Analytical Methods

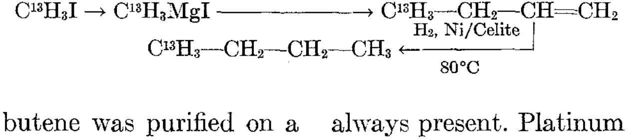
For reactions with ethane, analyses of the reaction mixture were done using a glass capillary leak to a MS10 mass spectrometer; methane and ethane were monitored from peaks at masses 16 and 30, respectively. Reaction mixtures from the butanes and neopentane were analyzed using a gas chromatograph with a flame-ionization detector, as previously described by Anderson and Avery (*4*). Two columns were used, (i) Pelletex/squalane, 20 m, operated at 35°C [Eggertsen, Knight, and Groennings (*7*)], (ii) dimethylsulfolane on 32–80 Celite, 20 meters, operated at 5°C [Frederick and Brooks (*8*)]. The latter was used in some cases for analysis in the C_5 and C_6 regions.

The products from the reaction of *n*-butane-1-C^{13} were analyzed by a combination of gas chromatography and mass spectrometry. The overall extent of reaction was followed in the usual way by the removal of 10-ml samples which were analyzed on the gas chromatograph. When the total *n*-butane had decreased by some 10–25%, the entire reaction mixture was transferred to the gas chromatograph, the effluent from which was led to a U-trap rather than the flame-ionization detector. By changing the U-trap according to the known retention times, the normal and isobutanes from the mixture were condensed in separate traps. The traps were packed with small glass Raschig rings and liquid nitrogen was used as the trap refrigerant. After warming to room temperature, the sample in a trap was examined mass spectrometrically using an MS10 mass spectrometer with about 50 V on the ionizing electrons. The sample was transferred from the trap, via a thoroughly evacuated soda-lime scrubber to a Toepler pump, whence it was compressed at the entrance to the spectrometer leak. The soda-lime was used to remove small but significant amounts of carbon dioxide which blank experiments showed were condensed from the atmosphere into the cold U-trap during its manipulation. After the mass spectral analysis, the residue of each sample was gas chromatographically analyzed to check the efficiency of the original separation. In no case was significant impurity found.

Materials

With the exceptions specified below, all hydrocarbons used either for instrument calibration or for reaction were Phillips Pure or Instrument Grade, and were purified on the vacuum line by trap-to-trap distillation. Isopentane was used as supplied, after outgassing by repeated freeze–pump–thaw cycling.

The preparation of *n*-butane-1-C^{13} was via the corresponding butene, the latter being made by the method of Reiger and Blue (*9*), with their apparatus reduced in size to accommodate a preparation on one-fifteenth of the scale described. Our apparatus included hypodermic transfer facilities. The reaction scheme may be summarized as follows:



$$\mathrm{C^{13}H_3I} \rightarrow \mathrm{C^{13}H_3MgI} \xrightarrow{\mathrm{CH_2{=}CH{-}CH_2Br}} \mathrm{C^{13}H_3{-}CH_2{-}CH{=}CH_2}$$

$$\mathrm{C^{13}H_3{-}CH_2{-}CH_2{-}CH_3} \xleftarrow[80^\circ\mathrm{C}]{\mathrm{H_2,\ Ni/Celite}}$$

The intermediate butene was purified on a Ward-Leroy still (*10*), since traces of allyl bromide poisoned the nickel catalyst. The purification of the final product was also done on a Ward-Leroy still. Gas-chromatographic analysis showed the total impurity to be 0.4%, this being mostly 1-butene with a trace of ethane. The overall yield, starting with 1 g of the methyl iodide was 40%. The methyl iodide was 62.4% C^{13} from Bio-Rad Laboratories.

Results and Discussion

Catalyst Structure

Transmission electron micrographs of platinum films deposited on mica [see Fig. 1(a)] and on sodium chloride [see Fig. 1(b)] showed microcrystalline structures, with average crystal widths of about 1200 Å. The average film thickness and thus the average crystal height is estimated at ~330 Å on mica and ~660 Å on sodium chloride. In both cases, crystals met along edges and there were no intercrystal gaps visible. Replicas of the surfaces showed that the tops of the crystals were generally flat and the intercrystal boundaries were only faintly apparent or could not be distinguished at all. Typical transmission electron diffraction patterns are shown in Fig. 1. In the case of the film on a mica substrate, the electron diffraction pattern [Fig. 1(a)] was obtained by scanning over most of the specimen area that was delineated within one grid area of a standard electron microscope grid. The relative intensities of the lines in the pattern obtained with a mica substrate clearly indicate strong crystal orientation with the (111) plane parallel to the substrate. On the 220 ring, six spots are faintly seen superimposed, thus showing that some of the crystals were similarly oriented with respect to each other about each ⟨111⟩ axis normal to the substrate. This feature varied, however, from specimen to specimen and was not always present. Platinum films deposited on glass at 450°C also showed evidence of (111) orientation with respect to the substrate. However, the degree of orientation on glass was less than on mica and the behavior was

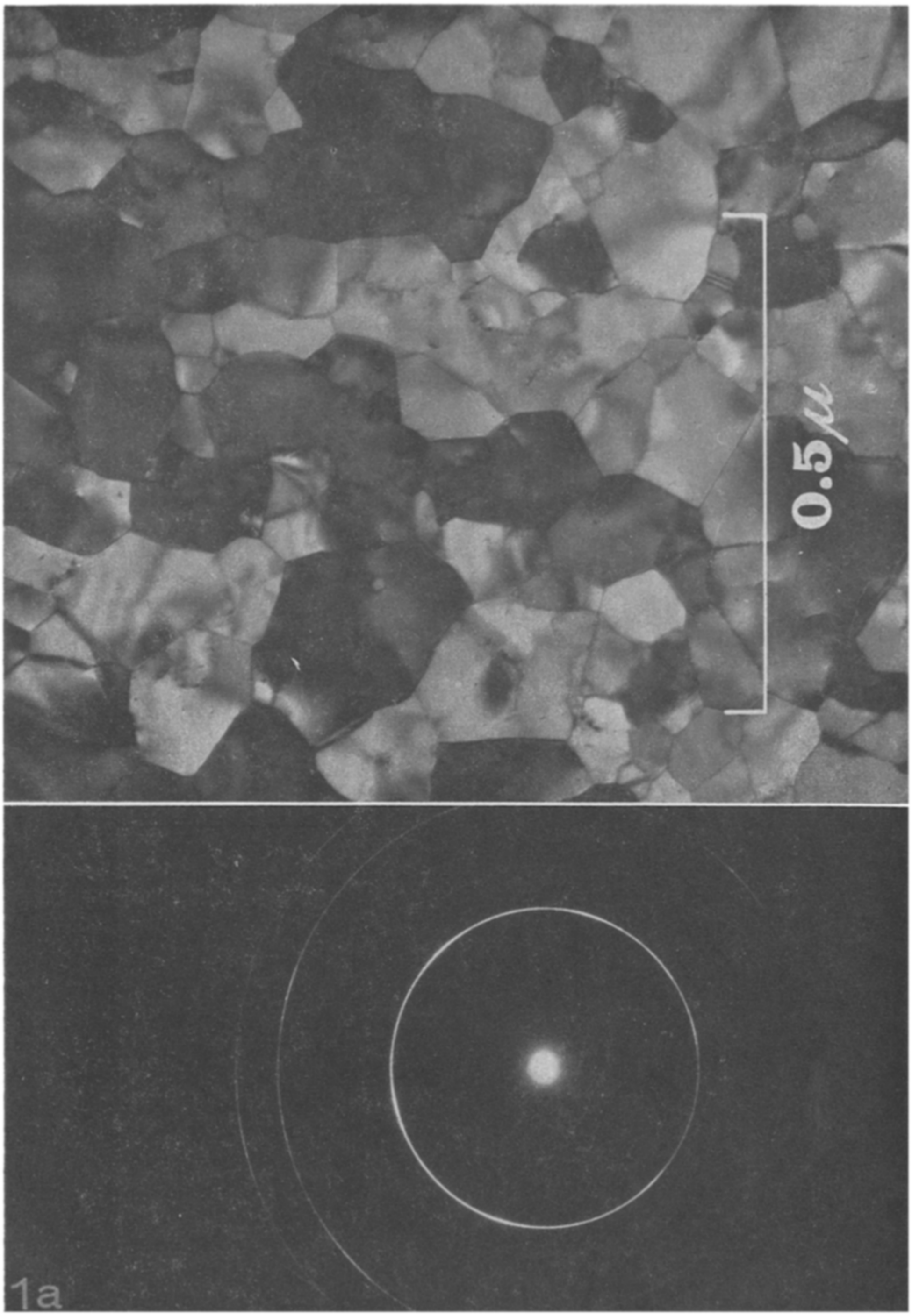


FIG. 1a

FIG. 1. (a) Top: transmission electron micrograph of platinum film deposited on mica at 400°C. Bottom: transmission electron diffraction pattern of platinum film deposited on mica at 400°C (specimen scanned). (b) Top: transmission electron micrograph of platinum film deposited on sodium chloride layer at 400°C. Bottom: transmission electron diffraction pattern of platinum film deposited on sodium chloride layer at 400°C; the area from which diffraction was obtained is shown in the inset as a micrograph.

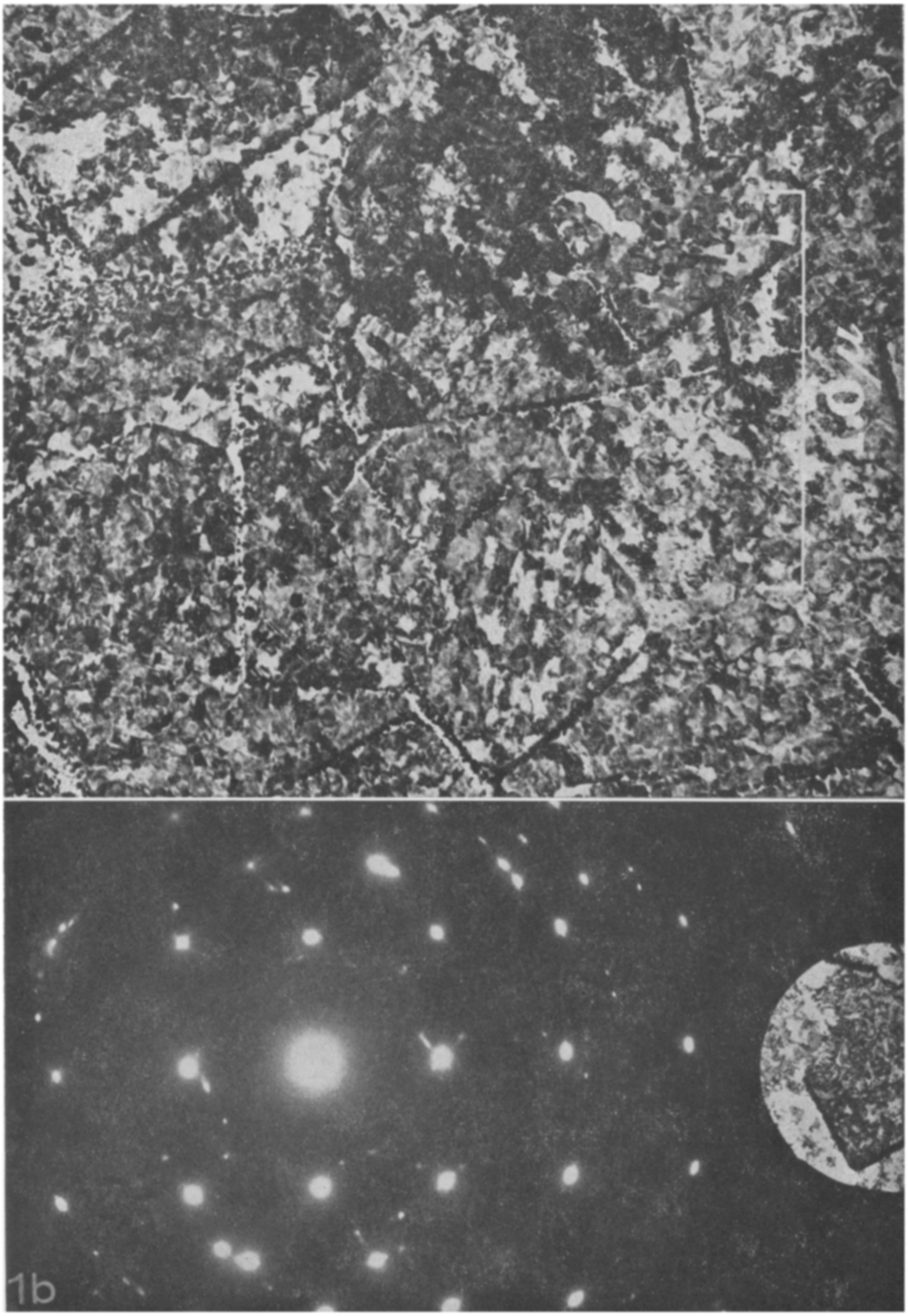


FIG. 1b

erratic, probably depending in an uncontrolled way on the history of the glass surface.

It is clear from the transmission micrograph in Fig. 1(b) that the crystals of sodium chloride each exposed a flat area about 10–20 μ across. It was thus possible to examine a diffraction pattern arising from platinum crystals on a single substrate crystal surface. Such a diffraction pattern is shown in Fig. 1(b) together with a transmission micrograph of the area from which it was obtained. This clearly shows that a substantial proportion of the platinum was present with the (100) plane parallel to the substrate and furthermore, most of the platinum crystals in such an area were similarly oriented with respect to each other about each ⟨100⟩ axis normal to the substrate.

From the diffraction results, taken in conjunction with the surface replicas, it was concluded that platinum films deposited on mica at 400°C and on sodium chloride at 400°C exposed predominately the (111) and (100) planes, respectively, to the gas phase. In comparison, platinum films deposited on glass at 0°C showed no significant orientation.

It should be noted that the method, first described by Beeck, Smith, and Wheeler (*11*) for the preparation of "oriented" films, which depends upon evaporation in the presence of an inert gas with a glass substrate at about room temperature, is quite unsatisfactory. Such films were examined in *transmission* by Anderson, Sanders, and McConkey (*12*) using 100-kV electrons for the thinner specimens and X-rays (α-Cu radiation) for specimens of maximum thickness, and little evidence for any orientation was found. The "orientation" that is evident from electron diffraction at grazing incidence apparently arises from a relatively few tall orientated crystals that project well above the average surface. This conclusion was confirmed by surface replication and is in agreement with the conclusions of Sachtler, Dorgelo, and van der Knapp (*13*), who also studied surface replicas. Furthermore it was evident from both replication studies that none of the crystals had tops that were parallel to the substrate.

Reactions with Unlabeled Alkanes

Reactions of ethane, *n*- and isobutane, neopentane and isopentane were studied over platinum (unoriented) and palladium, and reactions of *n*- and isobutane were studied over (111) and (100) platinum surfaces.

Reactions were generally limited to about 20% loss of parent hydrocarbon to minimize the influence of products on the course of the reaction. Rates of reaction and initial product distributions were estimated from the initial slopes of the composition versus time curves. With standard reaction mixtures (12/1 hydrogen to hydrocarbon), neopentane on platinum was the only system to exhibit appreciable self-poisoning, and here the reaction ceased after the consumption of about 15% of the parent; with the other hydrocarbons, the composition versus time plots were linear at least up to 20% loss of parent.

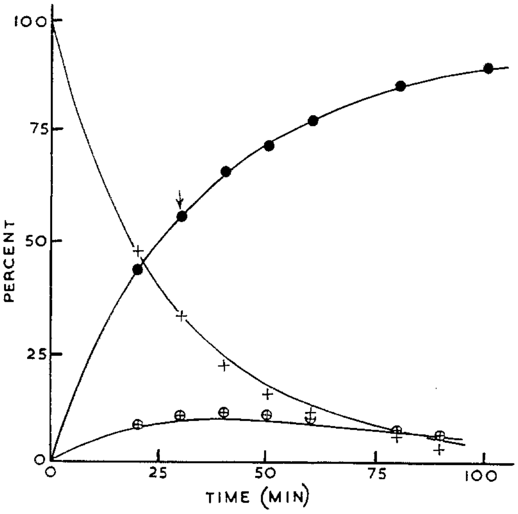
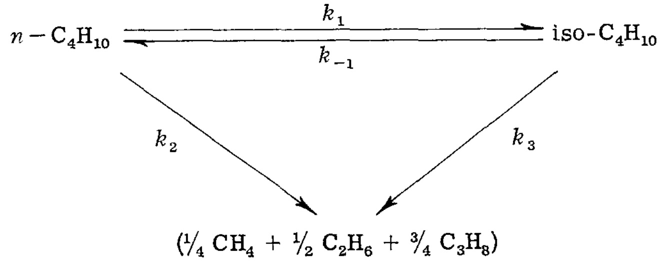


Fig. 2. Formation of products from reaction of *n*-butane on 10 mg of Pt at 296°C. Points experimental, curves calculated by method given in text. Experimental points and calculated curves were scaled together at the point marked by an arrow: +, *n*-C_4H_{10}; ●, (1/4 CH_4 + $\frac{1}{2}C_2H_6$ + 3/4 C_3H_8); ⊕, iso-C_4H_{10}.

Figure 2 shows composition versus time data for *n*-butane over platinum taken to a very high extent of reaction to illustrate the general course of reaction. In Fig. 2 the points are experimental, while the lines have been calculated for the reaction scheme



in which the hydrocracking products are expressed in C_4 equivalents. Small corrections have been applied to the experimental points to allow for the diminished reactant pressure resulting from the removal of samples. To calculate these lines we have used the appropriate integrated rate expressions derived by Wei and Prater (*14*) by matrix algebra methods, and inserted for k_1, k_{-1}, k_2, and k_3 *relative* values 1.00, 2.06, 4.35, 1.10, respectively. These values were obtained from the corresponding individual reaction rates measured by the initial slope method. The calculated lines were scaled to the experimental data at the single point marked on the figure. This calculation assumes that all of the contributing reactions are first order. The experimentally measured orders with respect to *n*- and isobutane are less than this (*vide infra*) so that complete agreement in Fig. 2 cannot be expected. However, the agreement is sufficient to validate the general reaction scheme and to confirm that the reaction remains unpoisoned even at a very high conversion. However, all reactions in which the hydrogen pressure was reduced from the standard value by a factor greater than 4 gave some evidence for self-poisoning.

Data for the dependence of reaction rates on temperature are summarized in Fig. 3 in the form of Arrhenius plots for standard reaction mixtures. The marked deviation from linearity of the curve for neopentane on platinum is attributed to the self-poisoning process already noted.

Activation energies, frequency factors, pressure dependence exponents, and product distributions are collected in Table 1. With the exception of ethane, pressure dependence exponents were determined from the effect on initial rates of up to fourfold reductions in reactant pressures. These exponents are each subject to an estimate uncertainty of ±0.2. The exponents listed for ethane were deduced from the fact that the disappearance of ethane (in a mixture containing a large excess of hydrogen) fitted a first-order rate law at least up to 80% conversions. The resulting exponent of unity is also subject to an estimated uncertainty of ±0.2.

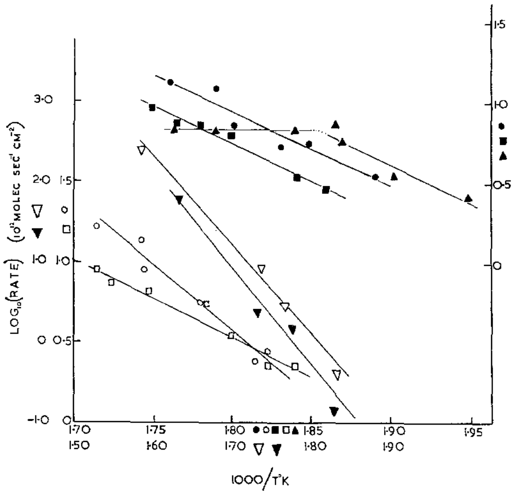


FIG. 3. Variation of reaction rate with temperature; all mixtures of standard composition: ▼, C_2H_6 on Pt; ●, *n*-C_4H_{10} on Pt; ■, iso-C_4H_{10} on Pt; ▲, neo-C_5H_{12} on Pt; ▽, C_2H_6 on Pd; ○, *n*-C_4H_{10} on Pd; □, iso-C_4H_{10} on Pd.

The pressure dependence data show that, relative to hydrogen, *n*- and isobutane were adsorbed much more strongly on palladium than on platinum. This difference between these metals was not, however, reflected with ethane. This suggests a different mode

TABLE 1
RESULTS FROM REACTIONS

	Metal[a]	Temperature range (°C)	Activation energy[b] (kcal mole^{-1})	$\log_{10}$ (frequency factor)[c] or rate (molecules/sec^{-1} cm^{-2})	Rate $\propto p^x_{\mathrm{HC}} \times p^y_{\mathrm{H_2}}$: x	y	Initial product distribution for standard reaction mixtures: CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}	iso-C_5H_{12}	n-C_5H_{12}	neo-C_5H_{12}
Ethane	Pt	274–340	57	34.2	1.0	—	100	—	—	—	—	—	—	—
n-Butane	Pt	256–300	21	21.1	0.7 (280°C)	1.4 (280°C)	32	29	28	11	—	—	—	—
Isobutane	Pt	265–299	21	21.0	0.5 (290°C)	1.4 (290°C)	24	6	20	—	50	—	—	—
Neopentane	Pt	239–295	21 (<270°C)[d]	21.2 (<270°C)[d]	—	—	14	5	4	10	3	59	5	—
Isopentane	Pt	278	—	Rate = 2.5 × 10^{12}	—	—	31	13	13	14	9	—	19	<1
n-Butane	(111) Pt	320–323	—	Rate = 1.4 × 10^{13}	—	—	30	30	28	12	—	—	—	—
Isobutane	(111) Pt	294–305	19	19.5	—	—	8	3	6	—	83	—	—	—
n-Butane	(100) Pt	300	—	Rate = 2.5 × 10^{13}	—	—	29	32	23	16	—	—	—	—
Isobutane	(100) Pt	299	—	Rate = 1.6 × 10^{13}	—	—	15	13	13	—	59	—	—	—
Ethane	Pd	273–358	50	31.9	1.0	—	100	—	—	—	—	—	—	—
n-Butane	Pd	276–310	38[e]	27.4[e]	−0.3 (290°C)	~0[f] (290°C)	45	13	41	1	—	—	—	—
Isobutane	Pd	270–311	21	21.0	−0.2 (294°C)	0.1 (294°C)	49	1	47	—	3	—	—	—
Neopentane	Pd	310	—	Rate = 9.0 × 10^{12}	—	—	49	3	6	35	7	—	—	—
Isopentane	Pd	310	—	Rate = 1.9 × 10^{12}	—	—	42	7	7	16	25	—	3	—

[a] Unoriented films where not otherwise specified.

[b] Estimated uncertainty ± 2 kcal mole^{-1}.

[c] Estimated uncertainty ± 0.5 in logarithm.

[d] Nonlinear Arrhenius plot.

[e] For standard reaction mixture; varies with $p_{\mathrm{H_2}}$ (see text).

[f] For $p_{\mathrm{H_2}} > \sim 45$ torr; varies with $p_{\mathrm{H_2}}$ (see text).

of adsorption of ethane compared with the butanes.

The approximate zero order with respect to hydrogen of the reaction of *n*-butane over ealladium held for hydrogen pressures in pxcess of the standard value; below this, the rate showed a nonlinear dependence on hydrogen pressure and passed through a maximum at about 30 torr. Because of the complex behavior, this was not investigated in further detail. There was also evidence that the activation energy for this reaction was dependent on hydrogen pressure, the measured value falling to 13 kcal mole^{-1} at a hydrogen pressure of about 20 torr.

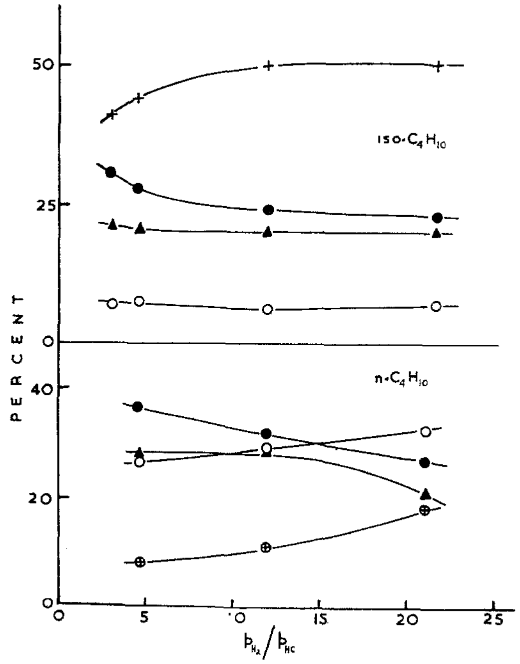


FIG. 4. Variation of product composition with hydrogen-to-hydrocarbon ratio (p_{H_2}/p_{HC}) of reaction mixture; reactions over platinum: ●, CH_4; ○, C_2H_6; ▲, C_3H_8.

The dependence of the proportions of initial products on reactant composition is shown in Fig. 4 for the reactions of the butanes on platinum. There was a decrease in the proportion of isomerization product at lower p_{H_2}/p_{HC} ratios, together with an increase in the proportion of methane. The latter illustrates the tendency to more extensive skeletal fragmentation of the hydrocarbon at lower hydrogen concentrations.

The proportion of isomerization product obtained from the reaction of *n*-butane on palladium was approximately constant at 1% for values p_{H_2}/p_{HC} in the range 9 to 20; however, below 9 the proportion of isomerization product was of poor reproducibility, but in the range 0.5% to 1.5%, and no trend could be distinguished. The reproducibility of the proportion of isomerization product from the reaction of isobutane over palladium was also poor but in the range 3% to 1% with a general tendency to decrease between these limits as the p_{H_2}/p_{HC} ratio was decreased from 20 to 4. The dependence of the proportions of initial hydrocracking products on reactant composition is shown in Fig. 5 for the reactions of the butanes on palladium. It is there seen that as the ratio p_{H_2}/p_{HC} decreased to about 4, there was a similar trend to that observed with platinum, namely an increasing proportion of methane in the products.

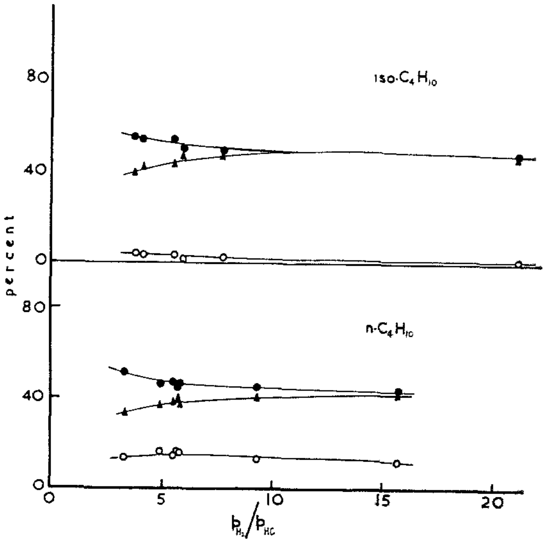


FIG. 5. Variation of product composition with hydrogen-to-hydrocarbon ratio (p_{H_2}/p_{HC}) of reaction mixture; reactions over palladium: ●, CH_4; ○, C_2H_6; ▲, C_3H_8; +, *n*-C_4H_{10}; ⊕, iso-C_4H_{10}.

With standard reaction mixtures, no olefins were detected in the reaction products. However, traces of olefins were detected in the products from reaction mixtures of composition $p_{H_2}/p_{HC} = 4$. These olefins, which were mainly dehydrogenation products of the parent hydrocarbons, did not exceed about 0.3% of the total products and have been neglected in recording initial product distributions. Reaction mixtures with $p_{H_2}/p_{HC} < 4$ were not studied in detail because olefin formation became a significant complication to the reaction path. It was noted, however, that over palladium, with $p_{H_2}/p_{HC} < 1$, the proportion of methane in the products was abnormally low; for instance, with $p_{H_2}/p_{HC} = 0.2$, the (% propane)/(% methane) $\simeq 3.5$ in the products. This can only be accounted for if carbon, which would otherwise be desorbed as methane, was being consumed in another reaction and for this, incorporation into the surface or bulk of the palladium catalyst is the most probable. To account in this way for the above methane deficiency requires the incorporation of about 6×10^{18} carbon atoms with the catalyst, corresponding with a 10-mg film to an average concentration of about 8%. Some direct evidence for the incorporation of carbon with palladium was obtained by the reaction of a mixture containing 2.85 torr of hydrogen and 17.2 torr of *n*-butane over an 18-mg film for 120 min at 320°C. After pumping away the reaction mixture, the catalyst was heated in 80 torr of hydrogen at 320°C for 120 min and this resulted in the return to the gas phase of 9×10^{18} molecules of methane. For comparison, a monolayer of carbon requires about 5×10^{17} atoms. Thus, if the methane deficiency were due to the deposition of surface carbon, this would have to be present at least to the extent of about 12 monolayers. For the catalyst to retain hydrocracking activity, it seems more likely that most of this carbon dissolves in the metal. No similar behavior could be found with platinum. These results are to be compared with those for reactions of methylamine and hydrogen ($p_{H_2}/p_{\text{amine}} = 1.4$), where at 207°C carbon was incorporated with palladium and platinum films to the extent of about 20% and 7%, respectively [Anderson and Clark (*15*)]. As pointed out by these authors, the main factor favoring carbon incorporation is probably the maintainance of a low hydrogen concentration on the surface. In the case of methylamine, this is achieved by the strong adsorption of methylamine and by the relatively easy desorption of ammonia which scavanges the surface of hydrogen. The behavior of palladium and platinum with respect to carbon incorporation in the reaction of the butanes is thus in agreement with the relative strengths of butane adsorption indicated by the pressure-dependence exponents in Table 1.

In view of our failure to detect carbon incorporation into platinum in hydrocarbon reactions, and since the present analytical technique shows that the methane analyses reported by Anderson and Baker (*3*) tend to be low, we conclude that those product distributions which were reported by Anderson and Baker (*3*) as deficient in methane (reaction of hydrocarbon plus excess hydrogen over platinum), resulted not from carbon incorporation into the catalyst, nor from a surface recombination of C_1 residues, but from analytical inaccuracy.

On palladium and platinum, product distributions were independent of temperature, within experimental error, indicating that the activation energies for hydrocracking and isomerization do not differ by more than about ±1 kcal mole^{-1}. All activation energies with the butanes and neopentane were in the range 19–21 kcal mole^{-1} (measured for reaction mixtures of standard composition), except for *n*-butane on palladium, for which the activation energy with a standard reaction mixture was 37 kcal mole^{-1}. However, the range between this latter value and the value of 13 kcal mole^{-1} found with a diminished hydrogen pressure, brackets the values found for the other systems. Activation energies for the reactions of ethane were much higher than for the butanes and this is similar to the behavior of these hydrocarbons over nickel and tungsten (*3*).

From the data in Table 1 one may calculate for the various systems the relative proportions of parent hydrocarbon reacting by isomerization and by hydrocracking. The values are summarized in Table 2. The activity of the (111) plane of platinum in promoting isomerization of isobutane was

TABLE 2
Relative Proportions of Isomerization and Hydrocracking with the Butanes

		(Isomerization rate) / (Hydrocracking rate)
Isobutane	(111) Pt	10.4
	(100) Pt	2.95
	unoriented Pt	2.08
	unoriented Pd	0.06
n-Butane	(111) Pt	0.23
	(100) Pt	0.39
	unoriented Pt	0.23
	unoriented Pd	0.02
Neopentane	unoriented Pt	3.64
	unoriented Pd	0
Isopentane	unoriented Pt	0.52
	unoriented Pd	0.06

exceptionally high. The proportion of isomerization from n-butane was on all surfaces lower than that of isobutane and there was no marked dependence on the crystal plane of the catalyst. In all cases platinum was very much more efficient in promoting isomerization than was palladium. At 278°C the equilibrium constant for n-pentane $\rightleftharpoons$ neopentane is 0.48 (API Project 44 data), so that the ratio (<0.05) of neopentane to n-pentane in the products from the reaction of isopentane over platinum was much less than equilibrium, and was clearly determined by kinetic factors.

The main features of the distributions of hydrocracking products given in Table 1 may be approximately accounted for on the assumption that in any particular molecule on the surface, only one carbon–carbon bond is broken. In the hydrocarbons studied, we shall distinguish five types of skeletal bonds to be broken: primary–secondary (1°–2°); secondary–secondary (2°–2°); primary–tertiary (1°–3°); secondary–tertiary (2°–3°); primary-quaternary (1°–4°). If p_x is the chance of a bond of type x being broken, the relative values of p_x may be chosen to reproduce the experimental distributions. The results are compared in Table 3. The agreement is least satisfactory with the pentanes, and this is probably the result of secondary reactions. It is important to note that these values of p are defined as empirical parameters on the basis that all bonds are of equal *a priori* accessibility. As will be seen later, this assumption is unlikely to be valid for the adsorbed reactant.

Reactions with n-Butane-1-C^{13}

Reactions were carried out over unoriented platinum films. In all experiments, the standard pressure of hydrogen was used

TABLE 3
Hydrocracking Products

		Relative bond rupture probabilities						Products (%)				
	Metal	$p_{1°-2°}$	$p_{2°-2°}$	$p_{1°-3°}$	$p_{2°-3°}$	$p_{1°-4°}$		C_1	C_2	C_3	iso-C_4	n-C_4
n-Butane	Pd	1.00	0.30	—	—	—	Calc	44	13	43	—	—
							Obs	45	13	42	—	—
Isobutane	Pd	—	—	1.00	—	—	Calc	50	—	50	—	—
							Obs	50	1	49	—	—
Isopentane	Pd	1.00	—	0.79	0.43	—	Calc	43	7	7	17	26
							Obs	43	7	7	17	26
Neopentane	Pd	—	—	—	—	1.00	Calc	50	—	—	50	—
							Obs	49	3	6	35	7
n-Butane	Pt	1.00	1.00	—	—	—	Calc	33	33	33	—	—
							Obs	36	33	31	—	—
Isobutane	Pt	—	—	1.00	—	—	Calc	50	—	50	—	—
							Obs	48	12	40	—	—
Isopentane	Pt	1.00	—	0.32	1.00	—	Calc	31	19	19	19	12
							Obs	39	16	16	18	11
Neopentane	Pt	—	—	—	—	1.00	Calc	50	—	—	50	—
							Obs	59	14	11	28	8

and details of hydrocarbon pressures are given later.

Mass spectral analysis showed that the labeled *n*-butane as prepared was 36.4% unlabeled, 61.6% singly labeled, and 2.04% doubly labeled. These data are in excellent agreement with those expected if account is taken of the C^{13} content of the methyl iodide and of the C^{13} natural abundance in the allyl bromide used in the synthesis: The expected figures are 36.36% unlabeled, 61.57% singly labeled, 2.04% doubly labeled, and 0.023% triply labeled. The agreement validates the assumptions used in this and other mass spectral analyses, namely that (i) the C_4^+ ions had mass spectral sensitivities that were independent of C^{13} content and (ii) the formation of fragment ions by the loss of hydrogens was independent of C^{13} content. Similar assumptions have been made and verified by Stevenson (*16*). Under the conditions used, loss of hydrogens provided fragment ion peaks in the following proportions relative to the mass 58 peak for *n*-butane parent (unlabeled): 57/58 = 0.19, and 56/58 = 0.060; while the corresponding ratios for isobutane were 0.96 and 0.12. In the following discussion, the term *n*-butane-1-C^{13} (62.4) refers to the material as prepared, with the composition given above.

Anderson and Baker (*3*) speculated that the butane isomerizations on platinum may have occurred by a recombination of adsorbed surface residues produced by fragmentation of the parent molecules. If these residues were mobile, this would lead to scrambling of the C^{13} in the isomerization product and also possibly in the parent. Scrambling would also occur if isomerization resulted from a surface bimolecular reaction between adsorbed C_4 residues. On the other hand, if isomerization occurred by a purely intramolecular rearrangement in a surface residue, no scrambling of C^{13} would result. The possible occurrence of C^{13} scrambling was examined by measuring the peak-height ratio of masses 60/59.

Data are given in Table 4 for the 60/59 ratios measured for *n*- and isobutane separated after reaction of labeled mixtures of standard composition. For this, the entire reaction mixture was fractionated. If C^{13} and C^{12}, present in the proportion of the labeled reactant, were randomly distributed among butane molecules, the following distribution would result: $4C^{12}$, 48.8%; $3C^{12}1C^{13}$, 38.4%; $2C^{12}2C^{13}$, 11.3%; $1C^{12}3C^{13}$, 1.48%; $4C^{13}$, 0.073%; and the 60/59 ratio expected for such a distribution is included in Table 4 for comparison. In computing this 60/59 ratio, allowance has been made for natural deuterium abundance and for fragmentation by loss of hydrogen. The results in Table 4 clearly show that there is no C^{13} scrambling and that the isomerization is entirely intramolecular. As a further check on this conclusion, a reaction was carried out using unlabeled isobutane in the presence of $C^{13}H_4$ to see if incorporation of C^{13} into the isomerization product could be detected. The reaction mixture contained isobutane (unlabeled), 4.8 torr; $C^{13}H_4$ (62.4% C^{13}), 3.2 torr; and hydrogen, 34.1 torr. The reaction was studied over unoriented platinum in the range 295–330°C. No incorporation occurred.

Were isomerization to occur by a simple methyl group migration, *n*-butane-1-C^{13} would lead entirely to isobutane-1-C^{13}

TABLE 4

60/59 RATIOS FROM LABELED REACTIONS

	Experiment 1 296°C[a]	Experiment 2 291°C[a]	Experiment 3 315°C[a]
Isobutane from reaction mixture	0.036 ± 0.002	0.033 ± 0.002	—
n-Butane from reaction mixture	0.034 ± 0.002	—	0.034 ± 0.002
n-Butane unreacted	0.034	0.034	0.034
Random distribution			
n-Butane	0.30	0.30	0.30
Isobutane	0.25	0.25	0.25

[a] 25% of parent reacted by hydrocracking and isomerization.

(peripherally labeled). Furthermore, there was the possibility of the production of *n*-butane-2-C^{13} from the *n*-butane-1-C^{13} during the reaction. For these reasons the position of the C^{13} atom in both the labeled *n*-and isobutane separated from the reaction mixture was determined by measurement of the 43/44 peak-height ratio in a manner similar to that used by Beeck *et al.* (*17*, *18*). This 43/44 ratio is mainly a measure of the ratio $[C_3{}^{12}H_7{}^+]/[C_2{}^{12}C^{13}H_7{}^+]$ of fragment ions produced from the butane in the ion source. For instance, if the chances of C^{12}–C^{12} and C^{12}–C^{13} bond rupture in the ion source were equal, and in the absence of rearrangements in the ion source, all the $C_3{}^+$ fragment ions from *n*- butane-2-C^{13} must contain a C^{13} atom, whereas from *n*-butane-1-C^{13} only half the $C_3{}^+$ fragment ions will contain a C^{13} atom. We present the results in terms of the 43/44 ratio as measured. For comparison, values of the 43/44 ratio have been calculated for specific types of labeled molecules and the calculations include corrections for (i) the presence of natural deuterium abundance, (ii) the effect of C^{13} on the chance of electron capture followed by fragmentation, (iii) contributions of fragment ions other than $C_3{}^{12}H_7{}^+$ and $C_2{}^{12}C^{13}H_7{}^+$ at masses 43 and 44, respectively, (iv) unequal chance of C^{12}–C^{12} and C^{12}–C^{13} bond rupture in the ion source. The work of Stevenson (*16*) showed that rearrangement in the ion source was negligible during the production of $C_3{}^+$ ions from the butane. The correction due to factor (ii) is very small and the figures of Stevenson (*16*) have been used. The basic data from which corrections for factor (iii) were obtained were 41/43 and 42/43 peak-height ratios for the unlabeled butanes. The respective values were 0.284 and 0.133 for *n*-butane; 0.435 and 0.362 for isobutane. The ratio (R), (chance of C^{12}–C^{12} rupture)/(chance of C^{12}–C^{13} rupture), was treated as a disposable parameter to account for the 43/44 ratio measured for *n*-butane-1-C^{13} (62.4). For this material the observed 43/44 ratio was 2.030 and this leads to $R = 1.12$. This may be compared with $R = 1.2$ given by Beeck *et al.* (*17*). The value of 1.12 has been used throughout this work for all the labeled hydrocarbons.

TABLE 5

43/44 RATIOS FROM ISOBUTANES

	Experiment 2 291°C[a]	Experiment 4 287°C[a]
Isobutane from reaction mixture	1.64 ± 0.03	1.63 ± 0.03
Isobutane-1-C^{13} (62.4)	1.61	1.61
Isobutane-2-C^{13} (62.4)	0.90	0.90

[a] 25% of parent reacted by hydrocracking and isomerization.

In Table 5 is given the 43/44 ratio measured for the isobutane recovered from the reaction mixture. For comparison are given the 43/44 ratios expected for isobutane-1-C^{13} (62.4) and isobutane-2-C^{13} (62.4). Since the reactant contained a significant proportion of doubly labeled material, the calculation of the 43/44 ratio for isobutane-1-C^{13} (62.4) and isobutane-2-C^{13} (62.4) was carried out assuming that they contained the appropriate proportion of doubly labeled isobutane. The data in Table 5 show conclusively that a methyl group in the 1-position of *n*-butane appears only in the 1-position in the isobutane isomerization product.

The 43/44 ratio of the labeled *n*-butane recovered from the reaction mixture was significantly different from the value for the unreacted parent. The 43/44 ratio calculated for *n*-butane-2-C^{13} (62.4) was 0.72, including a contribution from doubly labeled material. Since the corresponding value for the reactant was 2.030, the 43/44 ratio is sensitive to the presence of relatively small amounts of the 2-isomer. Experiments were designed so that 10-ml samples taken during the reaction were quantitatively analyzed on the gas chromatograph for components up to isobutane; the column effluent was then diverted so that the *n*-butane component was collected in a refrigerated trap for subsequent mass spectrometric examination. The proportion of *n*-butane-2-C^{13} in the *n*-butane fraction was related to the measured 43/44 ratio by the expression

$$\frac{[n\text{-butane-2-C}^{13}]}{[\text{total } n\text{-butane}]} = 0.555 - 0.273\ (43/44)$$

The results are collected into Fig. 6 which shows the ratio (P), (amount of *n*-butane-

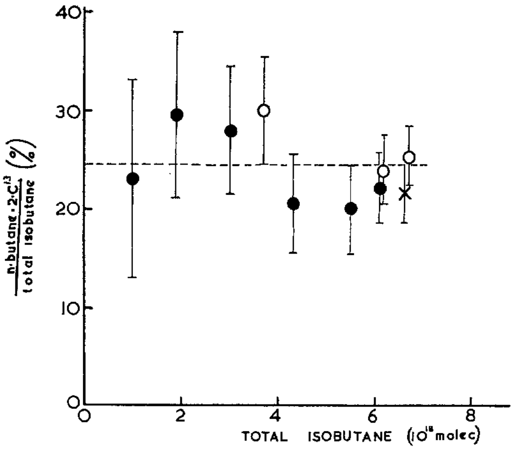


FIG. 6. Dependence of P, (amount of n-butane-2-C^{13})/(total amount of isobutane), on total amount of isobutane: ○, 5 mg Pt at 286°C, standard reaction composition; +, 11 mg Pt at 291°C, standard reaction composition; ●, 10 mg Pt at 310°C, reaction composition 1.90 torr n-butane-1-C^{13}, 44.5 torr hydrogen.

2-C^{13})/(total amount of isobutane), as a function of the total amount of isobutane formed in the reaction. In order to compute values of P, the total n-butane content of each 10-ml sample was needed. In these experiments the n-butane component was collected and its amount was thus not measured; it was therefore calculated from the known initial n-butane concentration and from the measured amounts of reaction products. Since it was desired to measure P to a high extent of conversion, in one experiment the pressure of n-butane-1-C^{13} (62.4) was reduced to 1.90 torr so that this could be achieved in a reasonable reaction time. The data from the experiment are distinguished in Fig. 6: the point for 6.2 × 10^{18} molecules isobutane corresponds to a total extent of reaction of 70%. The other data were obtained with mixtures of standard composition, and other reaction conditions are given in Fig. 6. The n-butane-2-C^{13} may be formed in two possible ways: (i) by a secondary reaction involving isomerization of isobutane-1-C^{13} previously formed, and (ii) by an isomerization of n-butane-1-C^{13} as a primary reaction. If process (i) were the only way in which n-butane-2-C^{13} were produced, it would follow that the ratio P should increase as the total isobutane increased. Figure 6 shows no such behavior within experimental error. It is useful, however, to make an estimate of the extent to which process (i) may contribute to P. Let us assume that on platinum n-butane and isobutane in a reaction mixture are adsorbed equally strongly, an assumption that is in approximate agreement with the pressure-dependence data of Table 1. Then, since the gas-phase composition during the reaction is known, we may calculate the amount of n-butane-2-C^{13} that would have been produced from the isobutane-1-C^{13} known to be present, using the previously measured initial rate data. The computed result is, for example, that at 70% overall reaction, 27% of the n-butane-2-C^{13} would come from process (i), while at 27% overall reaction, the proportion is 7%. The weighted mean of P from Fig. 6 is (23.6 ± 2)%, where each weighting factor was taken as the reciprocal of the square of the estimated error on each point. If a correction due to process (i) is applied, the mean value of P is 19.6%. In the absence of precise knowledge of the contribution from process (i), we adopt 20% ± 3% for the mean of P.

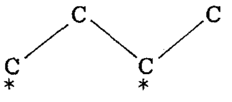
GENERAL DISCUSSION

Unless otherwise specified, this discussion refers to reactions over platinum, since isomerization was of much greater importance on this metal, and thus it was studied in greater detail. By the term *diadsorbed,* we mean bonding to the surface at two carbon atoms.

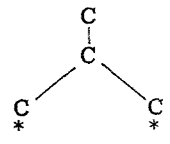
The present isomerization of, for instance, neopentane has a formal similarity to the Wagner-Meerwein type rearrangements studied by Whitemore and co-workers (*19, 20, 21*) with neopentyl halides. However, it is well established [cf. Ingold (*22*)], that these and other Wagner-Meerwein rearrangements proceed by a carbonium ion mechanism, and we reject the possibility of the existence of a carbonium ion as a discrete entity on a metal surface. The evidence, summarized, for instance, by Bond (*23*), clearly shows that the hydrocarbon–metal bond is essentially covalent, although the electronegativity of the metal may be sufficient to cause a fractional electron deficiency in the adsorbed residue relative to the gas-phase molecule.

Hydrocracking and skeletal isomerization had the same activation energy, and the amount of *n*-butane-2-C^{13} was in a constant ratio to the other product of skeletal isomerization (isobutane). We propose that all three processes proceed from a common surface intermediate. Below 270°C neopentane reacted with an activation energy and frequency factor very similar to those for the butanes, and since neopentane cannot form a 1–2 diadsorbed intermediate without prior fragmentation, it is reasonable to conclude that a 1–2 diadsorbed intermediate is not primarily involved in the butane reactions either. This is in agreement with the observation that ethane, which can only be diadsorbed in the 1–2 mode, reacted with a much higher activation energy than the other hydrocarbons. Anderson and Avery (*4*) discussed the possibility of a planar intermediate π-bonded to the surface in a manner similar to that suggested by Kemball *et al.* (*24*); this was rejected on the grounds that such an intermediate could not be formed from neopentane. It is improbable that the immediate surface precursor to the present reaction should be adsorbed at only a single carbon atom; it would be difficult to reconcile the substantial difference in reactivity of ethane and neopentane, or the marked effect of crystal plane with such a model. Furthermore, it has been suggested (*25*)—perhaps with little more than intuitive justification—that diadsorption (in the 1–2 mode) is a necessary precursor to carbon–carbon bond rupture. We shall proceed on the assumption that the surface precursor to the present reaction with the butanes is 1–3 diadsorbed.

If a 1-3 diadsorbed intermediate is formed, *n*-butane would give (A) and isobutane (B)

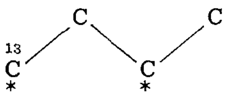


(A)

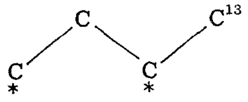


(B)

while *n*-butane-1-C^{13} would give two distinct structures depending on the position of the labeled atom.

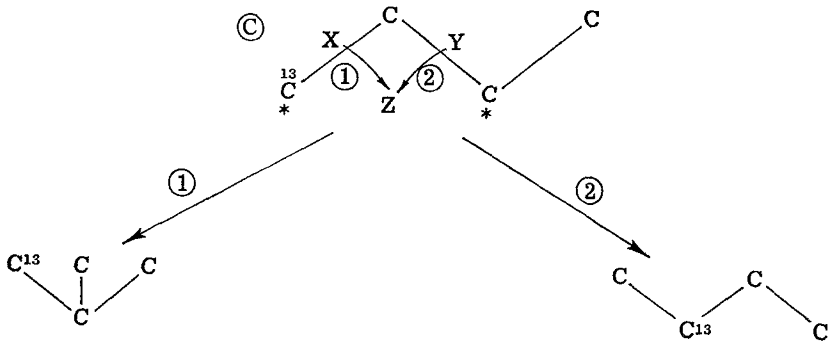


(C)



(D)

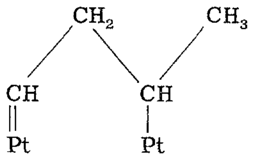
An atom bound directly to the surface is here designated by *; the symbol * does not, however, imply the use of any particular number of surface atoms, or of any particular number of adsorbate–adsorbent bonds. For simplicity, only the carbon skeletons are shown. Starting from the species (C) for instance, the isomerization reactions may be *formally* represented by



where the isomerization reactions are written as bond shifts from positions X or Y to Z. For hydrocracking to proceed from (C), rupture at X or Y must occur without the ultimate formation of a bond at Z, rupture at X leading to methane plus propane, rupture at Y to two ethanes. In such a residue as (C), the bond to the free methyl group is inaccessible to hydrocracking, and therefore to reproduce the observed product distribution (Table 3) would require $p_X/p_Y = 2$. The above scheme does not give a detailed description of the reaction path; that is, it says nothing about the transition state. It would clearly be reasonable to postulate that the reaction proceeds through a cyclic (adsorbed) transition state. However, it should be noted that this does not necessarily require the presence of an adsorbed cyclic intermediate, the latter term being used for a species of relatively long lifetime, as distinct from the transition state. In an attempt to verify or disprove the presence of an adsorbed cyclic intermediate, we have studied the hydrogenation of methylcyclopropane over platinum films under the same conditions as the present reactions (*26*). The distribution of reaction products was markedly different from that required to be consistent with the present results. We therefore tentatively conclude that a cyclic intermediate is not involved in the present reaction.

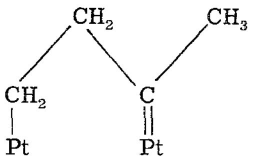
If the small amount of doubly labeled material in the *n*-butane-1-C^{13} (62.4) is neglected, and ignoring any isotope effect on the adsorption equilibria, *n*-butane-1-C^{13} (62.4) will yield proportions of residues (A):(C):(D) = 0.372:0.314:0.314. Reaction schemes similar to that shown for (C) may be written for (A) and (D). If a value is known for the ratio Q, (chance of bond shift from X)/(chance of bond shift from Y), P may be calculated. For this purpose, Q is defined without reference to isotopic composition; in the calculation we have assumed a 12% correction for a kinetic isotope effect. If we assume that $Q = p_X/p_Y = 2$, we obtain $P = 16.3\%$. This is close to the experimental value of P. There appears to be no means for making a more accurate *a priori* estimate of Q. To reproduce $P = 20\%$ requires $Q = 1.63$.

Anderson and Baker (*3*, *27*) suggested reasons why an adsorbed hydrocracking precursor is probably multiply bonded to the surface at least at one carbon atom. On this basis, species (A) may be more realistically represented as



(A 1)

or

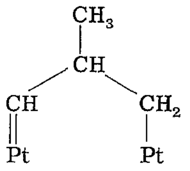


(A 2)

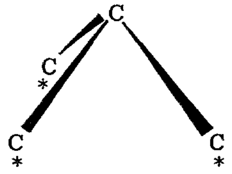
It may be noted that the corresponding surface residue from neopentane cannot accommodate a double bond except with the surface.

By taking the C–C distance as 1.54 Å and the C–C–C bond angle as 109.5°, the distance between the 1 and 3 carbon atoms is 2.52 Å. By allowing some twisting about C–C bonds, species such as (A1) and (A2) satisfactorily fit the nearest-neighbor distance on platinum of 2.76 Å.

The reactions of isobutane may be formulated in an analogous manner from species (B) or (B1)



(B 1)



(B 2)

However, in this case the symmetrical triadsorbed intermediate (B2) readily fits the (111) close-packed plane of platinum, and this we suggest to be responsible for the enhanced efficiency of the (111) plane for the isomerization of isobutane. In agreement with this, it will be seen from Tables 1 and 2 that on a (100) surface which ideally contains no such triangular arrays of sites, the proportion of isomerization of isobutane was not much different from an unoriented film.

It should be noted that, although triangular arrays of sites such as are required for (B2) occur (in smaller proportion) on other crystal planes [e.g., on (432)], the work functions of the various planes will differ and so will the bonding properties of the surface metal atoms. This would be even more apparent on planes such as (211) where the atoms in question are edge atoms on a step. The close-packed (111) plane would be expected to have the highest work function. It should be emphasized however, that properties such as work function and crystal parameter which do not describe the detailed bonding character of the surface metal atoms, do not necessarily form a satisfactory basis for correlations with catalytic activity. For instance, preliminary experiments with evaporated iridium films have shown that this metal has no isomerization activity and is much more active than platinum for hydrocracking, yet the nearest-neighbor distance in iridium is only 0.06 Å less than platinum and the work functions are 5.40 and 5.27 eV, respectively.

The isomerization of *n*-butane-1-C^{13} was studied by Beeck *et al.* (*18*) over a water-promoted aluminum bromide catalyst. However, this reaction clearly proceeds by a quite different mechanism to that over platinum, since the initial reaction product was reported to contain *n*-butane-2-C^{13}, isobutane-1-C^{13}, and isobutane-2-C^{13} in the same proportions as the ratios of their random statistical weights. This result was interpreted as deriving from a general activation of the molecule as a whole (as opposed to activation of only a specific part), very probably by a carbonium ion mechanism.

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