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LETTER TO THE EDITORS

The Isomerization of Isobutane and Neopentane over Evaporated Films of Platinum and Palladium

It was recently shown by Anderson and Baker (*1*) that, over evaporated platinum films at about 300°C, the butanes underwent isomerization (accompanied by hydrocracking) and that the platinum was the sole seat of catalytic activity. We wish to present a preliminary report of a comparative study of this reaction using isobutane and neopentane. Kemball *et al.* (*2*) suggested that for the polymethylcyclopentanes, *cis–trans* isomerization and deuterium exchange were most readily accounted for by assuming a planar intermediate π-bonded to the surface. With this in mind, the present experiments were designed to test whether the concept of a π-bonded intermediate could be extended to account for skeletal isomerization of alkanes. While this report was being prepared, Gault *et al.* (*3*) reported that skeletal isomerization of the hexanes could occur with platinum as the only catalytically active site and these authors suggested a π-bonded intermediate.

Experimental

The general technique and experimental conditions were the same as previously used (*1*), except that a flame-ionization detector was used with the gas chromatograph. The increased sensitivity made it possible to analyze the contents of 10-ml sample bulbs which were filled successively by expansion from the reaction vessel. With the total reaction volume of about 570 ml, up to 6 samples could be taken without serious disturbance of the quantity of material in the reaction vessel. Each component was estimated with an uncertainty of about 6%. This sample volume was sufficiently small that the gas could be compressed and injected onto the column without preliminary removal of excess hydrogen, as was previously necessary (*1*). Comparison with previous results showed that the procedure requiring the removal of excess hydrogen had generally resulted in methane being somewhat underestimated.

Results and Discussion

Reactions were studied in the range 265–310°C and most experiments were done with a standard reaction mixture containing a H_2/hydrocarbon molar ratio of 12/1. Reactions were 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 then estimated from the initial slopes of the composition vs. time curves.

Figure 1 shows data for the rate of reaction of parent hydrocarbon plotted as $\log_{10}$(rate) vs. $1/T$°K. The reaction of neopentane on platinum in this temperature range has an apparent activation energy of close to zero and we attribute this to a concurrent self-poisoning reaction, since it was also observed that the neopentane reaction ceased after about 15% of the parent hydrocarbon had reacted. No self-poisoning was apparent with isobutane, for which the activation energy was 21 kcal mole^{-1} on both metals.

Initial product distributions are contained in Table 1. The data for isobutane on platinum are generally similar to those reported previously at 284°C (*1*). However, from neopentane over platinum we have now identified a very substantial proportion of the isomerization product, isopentane, a compound to which G. L. P. C. analysis was not previously extended and which was thus not previously reported (*1*). In all cases, the

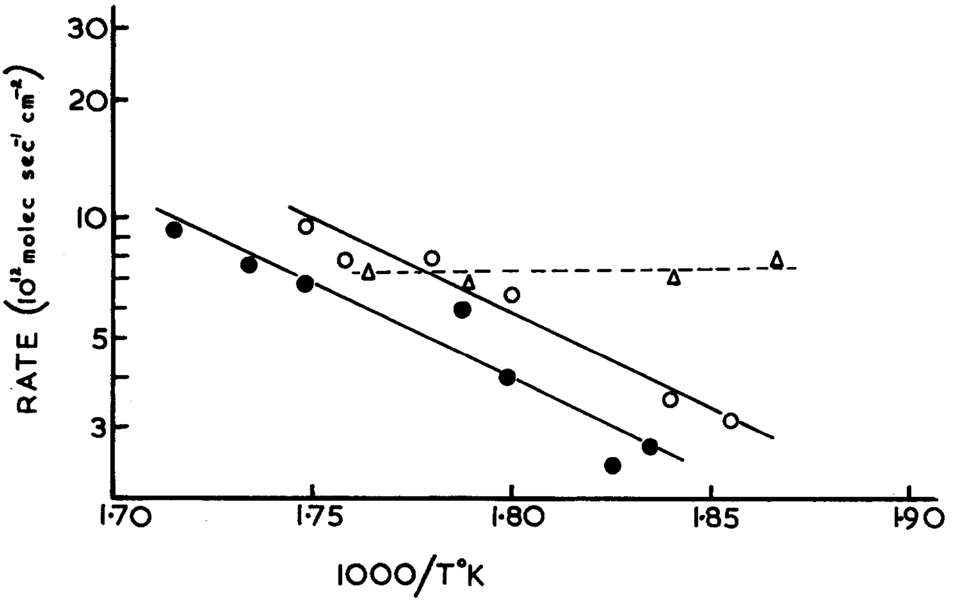

FIG. 1. Variation with temperature of rate of reaction (isomerization plus hydrocracking); H_2/hydrocarbon molar ratio 12/1 in all cases: ○, isobutane on platinum; △, neopentane on platinum; ●, isobutane on palladium.

product distributions were, within experimental error, independent of temperature over the range studied, so that isomerization and hydrocracking are thus characterized by the same activation energy. From the data in Table 1, the effect on the product distribution of decreasing the proportion of hydrogen in the reaction mixture is also apparent: With both hydrocarbons the result is to decrease the contribution of isomerization relative to hydrocracking.

The reaction of isobutane on palladium gave very much less isomerization than on platinum and the reaction is almost entirely that of hydrocracking at one carbon–carbon bond to give methane and propane.

Provided the hydrocarbon can assume the necessary planar conformation, an intermediate π-bonded to the surface has been suggested by Kemball *et al.* (*2*) as being the most reasonable interpretation for deuterium exchange and *cis–trans* isomerization data for hydrocarbons of more than two carbon atoms, particularly over palladium. This is an extension of the suggestion of a planar intermediate previously made by Anderson (*4*) to account for the racemization of (+)3-methylhexane. Now the essential fea-

TABLE 1
INITIAL PRODUCT DISTRIBUTIONS

Catalyst	Hydrocarbon	H_2/hydrocarbon ratio	Distribution of initial products (%)						
			CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}	iso-C_5H_{12}	n-C_5H_{12}
Platinum	Isobutane	12/1	24	6	20	50	—	—	—
		4.5/1	32	7	21	40	—	—	—
Platinum	Neopentane	12/1	14	5	4	3	10	59	5
		4.5/1	20	8	7	6	14	40	5
Palladium	Isobutane	12/1	49	1	47	3	—	—	—
		4/1	56	4	39	1	—	—	—

ture of such a π-bonded intermediate is that the molecule should have not less than three adjacent nonquaternary carbon atoms. Furthermore, from the data of Kemball *et al.* (*2*) it is clear that some of the required adjacent carbon atoms may, if necessary, come from methyl groups. Thus, isobutane would be capable of forming a π-bonded intermediate, but neopentane would not. Our observed isomerization of neopentane makes it certain that a π-bonded intermediate is not necessary for isomerization. Furthermore, the fact that neopentane and isobutane react over platinum at comparable rates and temperatures suggests that a π-bonded intermediate is not involved in the reaction of isobutane. In further confirmation of this, we note that although it was concluded (*2*) that π-bonded intermediates formed much more readily on palladium than on platinum, the data in Table 1 reveal that palladium is much less efficient in catalyzing the isomerization of isobutane than is platinum.

In the absence of a π-bonded intermediate for these reactions, one must presume that the adsorbed intermediates are bonded to the surface by σ-bonds; the possible types of surface species formed have been discussed previously (*1*, *5*). The present conclusions do not invalidate the concept of a π-bonded intermediate for exchange and *cis–trans* isomerization reactions at lower temperatures.

From the relative depression in the proportion of isomerization at a reduced hydrogen/hydrocarbon ratio, we conclude that isomerization is favored by maintaining a relatively high degree of hydrogenation of the adsorbed species, an increased degree of surface dehydrogenation leading to more extensive carbon–carbon bond rupture. This argues against the validity of a surface recombination mechanism for isomerization as suggested by Anderson and Baker (*1*), and while no conclusive evidence is at the moment available, we consider that the alternative of a bimolecular surface reaction should be considered. It should be possible to distinguish between these alternatives by an examination of the C^{13} distribution in the *n*-butane produced, for instance, from a mixture of light isobutane and isobutane-(C^{13}, C^{13}), provided the mobility of the adsorbed species is low. Such experiments are planned in this laboratory.

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