from thermodynamic considerations, cracked products should, of course, predominate in the reaction mixture with increasing temperature of reaction.

4. Effect of Change of Catalyst–Water–Hydrocarbon Ratio.—In Table IV are shown data of two types; first, varying amounts of water were added to varying weights of catalyst to give the same final water concentration, based on catalyst weight, and, secondly, a constant amount of water was added to varying weights of catalyst to give different final levels of water concentration. The amount of hydrocarbon added was constant in all experiments. Increasing the amount of catalyst containing a fixed percentage of water has little effect on the extent of reaction since the original catalyst-hydrocarbon ratio is quite large. However, varying the final water concentration of the catalyst does show a very marked effect on isomerization as has already been indicated by the data of Table II.

TABLE IV

EXTENT OF ISOMERIZATION AS A FUNCTION OF CATALYST–WATER–HYDROCARBON RATIO

Conditions: in all cases, 2.0 (gaseous) cc. of hydrocarbon was used. Reaction was for one hour at 100°.

Hydrocarbon	Wt. of catalyst, g.	Wt. of water added, mg.	Isomerization, %
2-MeC_5	2.0	12.0	3
	3.0	18.0	4
	5.0	30.0	4
	1.0	14.0	0
	2 0	14.0	3
	5.0	14.0	12

COMPARISON OF SILICA–ALUMINA WITH ALUMINUM CHLORIDE AS ISOMERIZATION CATALYSTS

Silica–alumina at 150°	Aluminum chloride at 100° [6]
Normal paraffins do not isomerize	Normal paraffins do isomerize
Interconversion of the methylpentanes is rapid	Interconversion of the methylpentanes is rapid
Formation of 2,3-dimethylbutane from methylpentanes is fairly rapid	Formation of 2,3-dimethylbutane from methylpentanes is fairly rapid
Formation of 2,2-dimethylbutane from 2,3-dimethylbutane does not occur	Formation of 2,2-dimethylbutane from 2,3-dimethylbutane does occur

In the paper by Evering and Waugh[6] from which these aluminum chloride data were taken, it was found that the slow step in the over-all isomerization of normal hexane shown below (taken from that paper) is the last step and the next slowest step is the first step. The two intermediate steps, interconversion of the methylpentanes and formation of the 2,3-dimethylbutane, are more rapid than the slower steps by two orders of magnitude. This, therefore, points up the possibility that the reason why the first and last steps are not seen with silica–alumina may relate to the kinetics of the reactions and not to any factor inherent in the catalyst.

STEPS IN ISOMERIZATION OF *n*-HEXANE

$$\begin{tikzcd} n\text{-}C_6 \arrow[d, shift left] \\ 2MeC_5 \rightleftarrows 3\text{-}MeC_5 \arrow[u, shift left] \arrow[d, shift left] \\ 2,3\text{-}Me_2C_4 \arrow[u, shift left] \arrow[d, shift left] \\ 2,2\text{-}Me_2C_4 \arrow[u, shift left] \end{tikzcd}$$

Acknowledgment.—The mass spectrometric data and their analyses are due to J. Terrell. Suggestions by other staff members aided in the interpretation of the results. Permission by the Houdry Process Corporation to publish is acknowledged with appreciation.

(6) B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

MARCUS HOOK, PA.

[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Reactions of C_5–C_8 Paraffins with a Silica–Alumina Cracking Catalyst.[1] II. Hydrogen Exchange

BY S. G. HINDIN, G. A. MILLS AND A. G. OBLAD

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Hydrogen exchange between a silica–alumina catalyst and C_5–C_8 paraffins was investigated. The isomerization and cracking reactions which these paraffins undergo have previously been determined (Part I). It was found that, at 150°, only paraffin molecules containing one or more tertiary carbon atoms exchange with catalyst hydrogen; normal paraffins and those containing only the quaternary structure do not exchange. All hydrogens exchange in molecules as 2-methylhexane, regardless of their distance from the tertiary carbon atom. The distribution of poly deuterated species formed parallels the statistical distribution calculated assuming equivalence of hydrogen and deuterium. Therefore, the adsorbed molecule remains on the catalyst surface before desorption for a period of time which is long relative to the time required for exchange. The total number of molecules which exchange is greater than the number which isomerize; and methyl group isomerization is not a required condition for exchange. A mechanism by which exchange occurs is presented. Exchange occurs with hydrogen atoms on the carbon atom alpha to the one bearing the positive charge and proceeds by migration of the positive charge along the hydrocarbon chain through intramolecular hydride ion-positive charge shifts. While formation of a catalyst hydrocarbon complex is the slowest reaction step, the observed products depend on the relative rates of the exchange, isomerization and cracking reactions, which are dependent on the hydrocarbon structure.

Hydrogen exchange reactions between cracking catalyst and hydrocarbons have proven very significant in pointing outt hose factors important in catalyst–hydrocarbon reactivity. Parravano, Hammel and Taylor[2] first reported exchange between methane and deuteromethane in the presence

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[1] Presented before the Petroleum Division, American Chemical Society, March, 1953.

[2] C. Parravano, E. F. Hammel and H. S. Taylor, THIS JOURNAL, **70**, 2269 (1948).

of a silica–alumina cracking catalyst. Hindin, Mills and Oblad[3] made a detailed investigation of the factors critical to the exchange between cracking catalyst and the butanes. Hansford, Waldo, Drake and Honig[4] studied the exchange of low molecular weight hydrocarbons with deuterium oxide in the presence of a cracking catalyst in some detail and examined also a few higher molecular weight hydrocarbons in exploratory fashion.

The present paper extends the range of paraffins studied in detail to the octanes. In the previous studies hydrocarbon structure has been found to be critical to the hydrocarbon–catalyst interaction. Therefore, the higher paraffins are of special interest since more varied structural isomers exist than are present in the butanes. The interpretation of the exchange data, together with the isomerization data presented in Part I, leads to a confirmation of previous conclusions regarding the mechanism of the exchange reaction and allows a broadening of this postulated mechanism. Moreover, a new suggestion is made to account for the observed activation of hydrogen atoms in the whole isoparaffin molecule, including those far removed from a tertiary carbon atom.

Experimental

Hydrocarbons used in this work and the experimental technique employed have been described in the preceding paper. Deuterium oxide of 99.8% purity was purchased from the Stuart Oxygen Company on allocation from the Atomic Energy Commission. The deuterated silica–alumina catalyst was prepared by adding deuterium oxide to dried Houdry S-45 catalyst in the manner already described.[3] Since it is difficult to prepare catalyst samples of exactly the same activity, the work reported here was carried out using a few large batches of catalyst. The deuterium of the deuterium oxide was approximately equal to the hydrogen of the hydrocarbon and to the deuterium remaining on the catalyst after drying; therefore, the total deuterium content of the system was about double that of the hydrogen content when using the higher molecular weight hydrocarbons and somewhat greater with lower molecular weight paraffins.

Interpretation of the Mass Spectral Data.—Complete analysis of the reaction product, which contains a wide variety of polydeuterated hydrocarbons, is not possible with present analytical techniques because of the number of species in the system. Thus, there are present the various deuterated species of the reactant hydrocarbon molecule, and also those of the isomeric molecules that were formed during reaction (see Part I). One can, however, obtain firm quantitative conclusions from the mass spectral data in terms of the *number* of deuterium atoms in the product molecules in the molecular weight range of the parent molecules without regard to their specific positions in the molecule or to the particular isomers present. These data are obtained from the parent mass peaks and are, therefore, not subject to the ambiguities associated with interpretation of fragment peaks. Briefly, the method of analysis is as follows: the mass spectrometer is operated at about three times normal operating pressure, to increase the absolute values of the peak heights. The parent mass peaks are corrected for the C^{13} isotope contents and the data are calculated, based on the following assumptions.

1. There is no contribution to a parent mass peak of a deuterated species by a more highly deuterated molecule. This means that, for example, in reaction with C_6H_{14} each mass in the range 86 to 100 (D_0–D_{14}) is assumed due to a single hydrocarbon species containing the number of deuterium atoms required to give the formula weight. Thus, it is assumed that the mass 100 peak arises only from C_6D_{14}; the mass 99 peak only from $C_6D_{13}H$ and so on. With isopentane, corrections were applied for masses lower than the parent mass, based on the fragmentation found for non-deuterated isopentane.

2. Sensitivities for all possible deuterated species are equal to those of the parent non-deuterated molecule.

These assumptions are obviously over-simplifications since the original hydrocarbons do show mass peaks attributable to loss of one or more hydrogens and, further, they do not take into account the sensitivities of the isomers formed. However, these fragmentation peaks due to loss of hydrogen are less than 20 to 30% of the parent mass peaks. Though the quantitative analysis may be in doubt, absolute accuracy is probably greatest with the most highly deuterated species, and it is primarily this range that is of major interest. Finally, regardless of the detailed interpretation of the product distribution, the fact that a mass peak of 100 appears from C_6H_{14}, for example, means that a C_6 molecule with 14 deuterium atoms in the *same* molecule is present.

This method of analysis is less accurate than that described by Stevenson and Wagner[5] in which the ionizing potential in the mass spectrometer is reduced to the voltage at which only the parent mass ion appears. However, with our instrument, the Consolidated Model 21-101, it is not possible to compensate for the decrease in sensitivity entailed by such procedure and the reading error of the chart becomes disproportionately large.

Results

Experimental results are presented in Table I where the amounts of the various deuterated species after reaction are shown. In Table II the distribution of products found experimentally for 2-methylheptane and 2,3-dimethylpentane is compared with that calculated assuming a statistical distribution of deuterium and hydrogen among that fraction of the hydrocarbon which reacted. A similar comparison is made in Fig. 1 for 2-methylheptane. In preparing Fig. 1, distributions were calculated using values of α (α = atoms D/atoms D + atoms H) varying between 0.5 to 0.7. Although a value of 0.57 for α was obtained from the experiment with 2-methylhexane, the calculated curve for $\alpha = 0.62$ is shown, which gives a somewhat better fit with the experimental data, especially for the most highly deuterated products. The difference of 0.05 unit in α is very likely within experimental error.

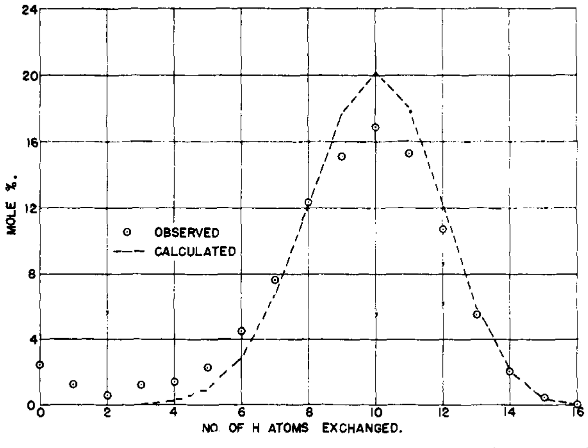

Fig. 1.—Exchange of 2-methylhexane and deuterated catalyst; comparison of observed distribution of products with that calculated assuming statistical distribution.

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[3] S. G. Hindin, G. A. Mills and A. G. Oblad, THIS JOURNAL, **73**, 278 (1951).

[4] R. C. Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947); R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, *ibid.*, **44**, 1108 (1952).

[5] D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).

TABLE I

HYDROGEN EXCHANGE BETWEEN PARAFFINS AND DEUTERATED CRACKING CATALYST

Conditions: 3.0 g. of deuterated catalyst dried for 1 hour at 525° except for runs with 2,3-Me_2C_5, 2,4-Me_2C_5 and n-C_7, in which cases the catalyst was dried at 315°; 15 mg. of D_2O ($\approx$0.5 wt. % on catalyst) + 2.0 cc. (gaseous) of hydrocarbon; reaction for 1 hour at 150°.

	Mole % of deuterated species formed									
Deuterated species formed	C_5H_{12} 2-MeC_4	C_6H_{14} 2-MeC_5	C_7H_{16} 2-MeC_6	C_8H_{18} 2-MeC_7	C_6H_{14} 2,3-Me_2C_4	C_7H_{16} 2,3-Me_2C_5	C_7H_{16} 2,4-Me_2C_5	C_7H_{16} 3,3-Me_2C_5	C_7H_{16} 2,2,3-Me_3C_4	C_7H_{16} n-C_7
D_0	6.4	12.8	2.5	2.7	21.6	38.4	29.7	>99	9.2	100
D_1	1.1	3.2	1.3	1.1	3.0	1.9	1.7	(after 4 hr.)	0.3	
D_2	1.2	0	0.6	0.5	1.0	0.6	0.6		0.2	
D_3	2.1	0	1.2	0.9	1.0	0.4	0.8		0	
D_4	4.9	0	1.4	1.9	2.1	0	0.7		0.3	
D_5	9.7	4.5	2.3	4.3	4.3	0	0.8		0.4	
D_6	15.9	3.2	4.5	6.8	7.7	0	0.7		0.6	
D_7	19.8	3.8	7.7	10.5	11.1	0.6	1.1		0.9	
D_8	18.9	3.2	12.3	13.6	12.9	1.0	2.4		1.7	
D_9	12.8	6.4	15.1	15.3	12.4	2.2	3.3		1.9	
D_{10}	5.8	7.7	16.9	14.2	9.9	4.6	6.0		3.3	
D_{11}	1.4	13.5	15.3	12.2	6.8	8.7	9.7		6.6	
D_{12}	0	18.6	10.7	8.4	4.0	11.9	12.6		12.3	
D_{13}		18.6	5.6	4.6	2.1	12.7	13.2		20.1	
D_{14}		4.5	2.1	2.3	0.1	10.8	10.7		23.9	
D_{15}			0.5	0.7		5.8	5.7		16.6	
D_{16}			0	0		0.4	0.3		1.7	
D_{17}				0						
D_{18}				0						
Max. no. H atoms exchanged	11	14	15	15	14	16	16	0	16	0

TABLE II

COMPARISON OF EXCHANGE DATA WITH CALCULATED STATISTICAL DISTRIBUTION BASED UPON THE ACTUAL FRACTION OF THE HYDROCARBON MOLECULES REACTING

No. of H atoms exchanged	2,3-Dimethylpentane Mole % exchange		2-Methylheptane Mole % exchange	
	Exptl.	Calcd.[a]	Exptl.	Calcd.[a]
0	38.4	..	2.7	...
1	1.9	..	1.1	...
2	0.6	..	0.5	0.1
3	.4	..	0.9	0.3
4	..	..	1.9	1.2
5	..	..	4.3	3.3
6	..	..	6.8	7.1
7	.6	.2	10.5	12.1
8	1.0	.7	13.6	16.7
9	2.2	2.1	15.3	18.5
10	4.6	4.9	14.2	16.7
11	8.7	9.1	12.2	12.1
12	11.9	12.9	8.4	7.1
13	12.7	13.5	4.6	3.3
14	10.8	9.9	2.3	1.2
15	5.8	4.5	0.7	0.3
16	.4	1.0	..	0.1
17	..	..	..	<0.1
18	..	..	..	<0.1

[a] Assuming statistical distribution.

In Table III, the percentage of molecules undergoing exchange is compared with the percentage undergoing isomerization as determined in separate experiments.[6]

Discussion

From the experimental results the following conclusions can be drawn as to effect of hydrocarbon structure on the exchange.

TABLE III

RELATIVE AMOUNTS OF EXCHANGE AND ISOMERIZATION

In 1 hour at 150°

		Reaction, %	
Hydrocarbon	H Exchange	isomerization	Cracking
2-MeC_4[b]	94	0[a]	3
2-MeC_5[b]	87	11	0
2,3-Me_2C_4[b]	78	9	5
2,3-Me_2C_5[c]	62	34	30
2,4-Me_2C_5[c]	70	13	36
3,3-Me_2C_5[b]	0	0	0
n-C_6[b]	0	0	0

[a] Isomerization to the "3-methyl" position would not be apparent. [b] Catalyst dried at 525°. [c] Catalyst dried at 315°.

1. n-Paraffins and hydrocarbons containing two methyl branches on the *same carbon atom* (and without an additional tertiary carbon) show no exchange under the experimental conditions.

2. For the monomethylalkanes all primary and secondary hydrogen atoms of the structure, *however far removed from the chain branch*, can exchange with deuterium of the catalyst (+ D_2O). In the case of 2-methylpentane, the tertiary hydrogen also underwent exchange. In the case of 2-methylbutane, 2-methylhexane and 2-methylheptane, one or more hydrogens appeared not to undergo exchange. A lack of exchange was found for the tertiary hydrogen of isobutane.[3] It should be noted, however, that if the distribution of products is of a statistical nature as indicated in Table II, the amount of the completely deuterated species in these experiments is expected to be so small that they would escape detection. In view of the results with 2-methylpentane, it appears that exchange of a tertiary hydrogen can occur, although perhaps at a slower rate than with primary or secondary hydrogens.

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(6) S. G. Hindin, A. G. Oblad and G. A. Mills, THIS JOURNAL, **77**, 535 (1955).

3. From the above discussion, therefore, it appears that the distribution of polydeuterated species parallels the statistical distribution that can be calculated assuming equivalence of deuterium and hydrogen.

4. Hydrocarbons with two branches on *separate carbon atoms* exchange *all* hydrogen of the structure. Comparison of the analytical results for 2,3-dimethylbutane with the calculated statistical distribution (Table II) shows that the distribution found experimentally closely parallels that calculated.

5. Of the hydrocarbons containing both a tertiary and a quaternary carbon atom only 2,2,3-trimethylbutane gave sufficient uncracked product for analysis and in this case, as seen in Table I, all hydrogen exchanged. Only about 1% of the heptane remained uncracked but this was sufficient to show the pattern of the exchange reaction.

6. When reaction occurs, the total number of molecules showing hydrogen exchange is always greater than the number isomerizing (Table III).

As pointed out previously, three reactions steps are necessary to the exchange reaction: (1) initial complex formation between catalyst and a hydrocarbon molecule, (2) exchange of hydrogen between catalyst and complex, and (3) release of a deuterated molecule by a new hydrocarbon through hydride ion transfer between the new hydrocarbon molecule and the deuterated complex.

The carbonium ion can be formed by reaction of an olefin with a catalyst Brönsted acid or by reaction of an isoparaffin with a catalyst Lewis acid.[3,4] Presumably the difference in reactivities between *n*- (and quaternary) and isoparaffins, seen both in the data in Table I of this paper and Table I of the previous paper, are related to the difficulty of initial formation of the primary or secondary carbonium ion from the *n*-paraffin, since, as has been shown,[7] a tertiary carbonium ion is more stable than a secondary carbonium ion by some 10–15 kcal.

Once the carbonium ion has been formed, the products observed depend not on thermodynamic equilibrium but on the relative rates of the other two steps: reaction of the carbonium ion on the catalyst surface, and desorption of the adsorbed hydrocarbon back into the gas phase.

Mechanism of the Exchange Reaction.—The most significant observation in the present experiments is that with 2-methyl paraffins. As seen in Table I, hydrogens attached to all carbon atoms exchange, however far removed those carbon atoms are from the tertiary carbon atom. For example, hydrogen on carbon six of 2-methylhexane exchanges, despite the fact it is the fourth carbon away from the chain branch. This leads to the question—how is it possible to activate all the hydrogen atoms in a long hydrocarbon chain?

That hydrogen exchange occurs between the catalyst and carbonium ion means that hydrogen atoms of the hydrocarbon (except perhaps the tertiary hydrogen) are equivalent to those of the catalyst. Hydrogen atoms of the catalyst are positive because of the strongly polarized O–H bonds. The effect of the positive charge of the carbonium ion, therefore, is to transfer to the hydrogen atoms definite positive character. This effect of charge redistribution might appear in one of two ways: (1) a general electronic activation of the entire carbonium ion on the catalyst surface, or, (2) an effect extending mainly only to those hydrogen atoms on the carbon α to the carbon atom bearing the positive charge.

The second possibility seems to us to be the more likely since the former, involving as it does the activation of an entire molecule containing only single bonds, would not be consistent with known organic reactivity.

If only the hydrogen atoms immediately adjacent to the positively charged carbon atom become activated for exchange, then, since all hydrogen atoms (excepting possibly the tertiary hydrogen) exchange, movement of the positive charge up and down the chain would be required. Methyl group isomerization cannot account for the observed exchange, for example, 87% of all molecules exchange compared to only 11% isomerization for 2-methylpentane, Table III (shift to 4-methylpentane would not be detected). We believe, therefore, that the movement of charge is accomplished primarily through intramolecular hydride ion shifts, rather than methyl group rearrangement, though the latter do occur. Unequivocal proof that methyl group isomerization is not a necessary requisite for exchange is seen in a number of experiments carried out using 2-methylheptane; no 4-methylheptane was found in the product, yet extensive exchange involving hydrogen of at least six carbon atoms took place. Exchange is believed, therefore, to occur as follows: the effect of the positive charge extends primarily to the hydrogen atoms on the carbon atoms alpha to the tertiary carbon atom, and these "α" hydrogen exchange with catalyst hydrogen. Once these hydrogen have exchanged, the positive charge can then transfer to the carbon α to its original position (the carbon on which exchange has just occurred) by intramolecular hydride ion shift. On this next carbon atom it then activates for exchange the hydrogen atoms on the carbon now α to it which were β to the tertiary carbon atom in the original carbonium ion. By this means through such intramolecular "hydride ion"–positive charge interchanges, the positive charge can move up and down the entire hydrocarbon chain and in so doing it activates all hydrogen of the structure for exchange with catalyst hydrogen. Concomitantly with this "hydride ion"–positive charge interchange, methyl group isomerization also occurs, but to a lesser extent than does the hydride ion isomerization, perhaps because of the greater mass of the methyl group relative to the hydride ion.

It may be noted that this shift of charge along the hydrocarbon chain means that another portion of the hydrocarbon chain is "attached" to the catalyst with time. This means either that there is a shift of the whole hydrocarbon each time the charge shifts, so that the molecule is attached to the same active site on the catalyst; or, a shift in position of the active site with the shift in charge distribution in the hydrocarbon molecule.

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[7] D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, THIS JOURNAL, **74**, 3269 (1952).

It had been hoped to obtain data on this assumed movement of charge by studying exchange reactions of hydrocarbons with a quaternary carbon in the chain in addition to a tertiary carbon, such as 2,3,3-trimethylpentane, and determine the extent of exchange on carbons 4 and 5 since this would involve a 1,3-shift of charge. However, this compound was largely cracked under the reaction conditions used (Table I, ref. 6) and no clear picture was obtained. 2,2,3-Trimethylbutane did show that all sixteen hydrogen atoms exchange (Table I). However, this is not a critical test since here the possibility that a shift of a methyl group occurred to give the "2,3,3" compound may explain the observed exchange on carbon 4. We hope at a later date to study larger hydrocarbon molecules, as 2,2,3,3,4-pentamethylpentane, and molecules of the camphane type, at lower reaction temperatures; in the former case, to see if the presence of two adjacent quaternary carbon atoms in the chain will affect isomerization and exchange; in the latter case, there is no possibility for methyl isomerization from the tertiary carbon.

Desorption of the Complex.—From the observation that deuterated species appear in statistical distribution for those molecules which have reacted (Fig. 1), one may conclude that the adsorbed molecule resides on the catalyst surface for a period of time which is long in comparison with the time required for the exchange reaction itself, and that during a residence on the catalyst surface, most, if not all, of the hydrogen atoms of the hydrocarbon exchange with catalyst hydrogen. Further, since a primary or secondary carbonium ion would be an extremely strong acid and would tend to saturate itself by hydride ion transfer from a second hydrocarbon molecule to a greater extent than would a tertiary carbonium ion, it must be assumed that the existence of such charged ions is for a period on the average less than the time required for hydride ion transfer from a second hydrocarbon molecule.

Now consider the mechanism by which desorption of the deuterated carbonium ion occurs, taking the exchange with isobutane[3] as an example. Take the first carbonium ion formed, the deuterated *t*-butylcarbonium ion. This can desorb from the catalyst only by abstracting a hydride ion from a second isobutane molecule, then appearing in the gas phase as $(CD_3)_3CH$. A second deuterated *t*-butylcarbonium ion can desorb by reacting with this partially deuterated molecule by abstracting either one of the primary deuterium atoms with its attached electron pair or by abstracting the tertiary hydrogen with its electrons. Since a primary carbonium ion is an extremely strong acid, the overwhelming tendency would be to lose the tertiary hydrogen rather than a primary deuterium atom.

Now, however, consider the exchange with isopentane (Table I), again looking at the second deuterated carbonium ion. It now has a choice of picking up either a tertiary hydrogen atom, two secondary deuterium atoms, and nine primary deuterium atoms. Since the secondary carbonium ion is not as strong an acid as is a primary carbonium ion, there is then the possibility that one of the deuteriums will be lost to the carbonium ion, giving rise to a completely deuterated isopentane. With isohexane and longer hydrocarbon chain systems, the number of secondary carbon atoms increases and, therefore, the possibility of losing a secondary deuteride ion becomes greater.

That very highly deuterated species appear in the gas phase is evidence of mobility of positively charged bodies on the catalyst surface. This arises, as follows: with this catalyst, whose surface area is about 300 $m^2/g.$, there is, on the average only one deuterium atom per 50 Å.^{2} of surface, at a 1% level of "water" content. Therefore, for a gas molecule as isobutane, whose cross-sectional area is about 35 Å.^{2} to become completely deuterated in a residence on the surface, either the adsorbed molecule sweeps out a fairly large amount of surface before desorption or, deuterons on the catalyst flow into the sphere of influence of the carbonium ion, or, that both occur fast enough so that fresh deuterons are always available for exchange.

The parallelism seen in Table III on the critical influence of hydrocarbon structure upon reactivity for exchange, isomerization and cracking is convincing evidence that some one mechanism is common to these reactions. Almost certainly the common controlling step is the formation of the polarized complex, designated as a carbonium ion, by the interaction of the hydrocarbon and the catalyst. The observed products are then dependent upon the relative rates of reactions possible to the carbonium ion–hydrogen exchange, isomerization, cracking—which rates depend upon the particular structure of the hydrocarbon.

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