above conditions, which is verified by the experimental results. At lower temperatures (10–12°) an appreciable yield of the *cis* isomer was obtained, because of the decreased solubility of the *cis* form. Table II, solutions 1-B and 2-B, shows that at low temperatures both *cis* and *trans* isomers are formed. It becomes obvious that under the above conditions the presence of the chloride ion is not necessary for the formation of the *cis* isomer.

Acknowledgment.—The authors are indebted to the Office of Naval Research for the sponsorship of this and continuing investigations.

Summary

1. The reactions between [$Pd(NH_3)_2Cl_2$], ammonia and sodium nitrite in aqueous solution were investigated with respect to the effect of variations in temperature, concentration of palladium, nitrite ion, ammonia and chloride ion.

2. Cold concentrated palladium solutions containing chloride ion favor the formation of the *cis*-dinitrodiammine palladium(II) isomer.

3. The *cis*-dinitrodiammine isomer in solution slowly reacts in a stepwise manner with ammonia and nitrite ion to form the *trans* isomer.

4. The ammonia and nitrite ion concentrations have relatively little effect upon the product formed.

5. The effect of pH may be of minor importance, low pH values favoring *trans* formation.

6. Small yields of the *cis* isomer were obtained in the cold by the action of ammonia upon the nitropalladite.

7. A mechanism is postulated which can explain all of the observed phenomena only if *trans* elimination is assumed.

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[CONTRIBUTION FROM HOUDRY PROCESS CORPORATION, MARCUS HOOK, PA.]

Hydrogen Exchange between Cracking Catalyst and the Butanes[1]

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

It is now established that oxide cracking catalysts are "acidic" in nature and that the "acidity" is responsible for the activity of this group of catalysts.[2a,b] The polarized complex (carbonium ion) theories, which have been successful in correlating the mechanisms of acid catalysis, have also been successful in explaining the chemistry of catalytic cracking in a general way.[2b,3] However, more detailed information on the nature of the catalyst–hydrocarbon complexes and the mechanisms of hydrogen transfer reactions is needed to establish the specific reaction of the catalyst with hydrocarbons. A study of the exchange reactions occurring between the cracking catalyst and hydrocarbon molecules offers such opportunity since it has been shown that cracking catalysts promote hydrogen exchange between water and hydrocarbons at temperatures far below those at which cracking occurs.[3,4]

A general study was made of the hydrogen exchange reactions of a typical silica–alumina cracking catalyst with various hydrocarbon classes. The results confirmed the general findings of Hansford[3] concerning the relative temperatures required for the exchange. In order to measure the factors critical to the exchange, a more detailed study was made with *n*-butane and isobutane. The C_4 paraffins were chosen because, of the paraffins which contain hydrogen atoms linked to primary, secondary, and tertiary carbon atoms, the butanes have the lowest molecular weight and are, therefore, the least complicated for analysis. Furthermore, it is necessary that any complete theory deal adequately with the generally unreactive paraffin molecule. Two effects were looked for: one, to ascertain the effect of structure of the paraffin on reactivity and, two, to determine the effect of other reagents, water, olefin and air on the exchange.

The general experimental procedure was either to contact the paraffin with a silica–alumina cracking catalyst that had been enriched with deuterium or to contact the silica–alumina cracking catalyst containing hydrogen with the monodeuterated hydrocarbon. The reaction time and temperature were chosen on the basis of preliminary work as one hour at 150°. After reaction, the hydrocarbon was removed and analyzed by means of a mass spectrometer. The effect of other agents was followed by incorporating them into the reaction mixture.

Experimental

Preparation of Reagents.—Isobutane, research grade, from Phillips Petroleum Co., was treated with anhydrous aluminum bromide at 0° to remove possible traces of olefins. Individual samples, 11.2 cc. (S.T.P.), were sealed into break-seal ampules under high vacuum conditions and used as needed. Normal butane, research grade, from Phillips Petroleum Co., was used without further purification.

Two monodeuterated isobutanes were prepared, one in which the deuterium was attached to a primary carbon atom, and the other in which it was attached to the tertiary carbon atom. They were prepared by means of the Grignard reaction. Solvent used in the preparation was removed by low-temperature distillation of the hydrocarbon in a Podbielniak column. Since preliminary work had indicated that little exchange was found at 50°, the hydrocarbons were further treated to remove possible olefin contaminants by passage through a bed of silica–alumina catalyst maintained at that temperature. The 2-methylpropane-2-*d* was further treated by passage through 98% sulfuric acid.

The deuterated silica–alumina cracking catalyst was prepared in the following manner: 50 g. of a standard synthetic silica—12.5 wt. % alumina cracking catalyst (Houdry

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[1] Presented before the Division of Petroleum Chemistry, American Chemical Society, September, 1950.

[2] (a) Yu. A. Bitepazh, *J. Gen. Chem.* (*U. S. S. R.*), **17,** 199 (1947); C. L. Thomas, *Ind. Eng. Chem.*, **41,** 2564 (1949); M. W. Tamele, Symposium "Heterogeneous Catalysis," Faraday Society (1950); G. A. Mills, E. R. Boedeker and A. G. Oblad, THIS JOURNAL, **72,** 1554 (1950). (b) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **41,** 2573 (1949); T. H. Milliken, G. A. Mills and A. G. Oblad, Symposium "Heterogeneous Catalysis," Faraday Society (1950); A. N. Titova, *J. Gen. Chem.* (*U. S. S. R.*), **17,** 673 (1947).

[3] R. C. Hansford, *Ind. Eng. Chem.*, **39,** 849 (1947).

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

Type S-45) originally calcined at 730° was dried for 1 hour at 525 ± 10°, under vacuum, to remove the small amount of water which had been picked up on standing. In all evacuations the pressure was reduced to 10^{-3} mm. or lower. After cooling, about 5 ml. of 90% D_2O was allowed to diffuse over into the catalyst bed while the entire system was maintained free of air. This wetted catalyst was redried for 1 hour at 525° and then a further 5 ml. of 99.8% D_2O admitted to it. Samples of this wetted catalyst (3.5 g.) were weighed out and held in tightly stoppered tubes until used.

Experimental Technique.—All exchange reactions were carried out using high vacuum technique. Fresh samples of catalyst and hydrocarbon were used for each experiment. The experimental procedure used was as follows: a break-seal ampule containing the hydrocarbon and a tube containing either air or olefin were sealed into the reaction tube ($\sim$50 cc. volume), the catalyst added, and the reaction tube sealed into the vacuum system. It was immediately pumped out and tested for leaks with a Tesla coil. There was, undoubtedly, a small amount of water pickup by the catalyst during the handling. This would tend to dilute slightly the deuterium content of the deuterated catalyst, but duplicate experiments with the same batch of catalyst indicated that such pickup did not affect exchange values within the experimental error.

After the reaction tube had been shown to be free of leaks, a furnace was placed around the bed of catalyst and the sample held at the predetermined temperature for 1 hour while under vacuum. The furnace was removed after the heating period, and the tube sealed off while still hot. The tube and contents then were held overnight at room temperature and again tested for leaks the next morning. If no leaks appeared, a slug was used to break the tube containing the air (or olefin) and then the saturated hydrocarbon.

The tube then was placed in a furnace held at 150 ± 2°. After 1-hour reaction time, a side tube, which was of 3 mm. mass spectrometer size, while still warm was plunged into a liquid nitrogen bath and held there until the catalyst bed had cooled to room temperature. The tube was then sealed off and the contents analyzed with the mass spectrometer. This particular technique was used to facilitate desorption of the hydrocarbon from the catalyst.

Experimental Data.—The mass spectrometric analyses were made using Consolidated Engineering Instrument, Model 21-101. Experimental results are reported in terms of "% exchange," where this value is the total mole % of all the deuterated butanes in the product gas and equals [100 minus mole % C_4H_{10}], or, for reactions between catalyst and monodeuterated hydrocarbons, equals [100 minus mole % C_4H_9D]. It is not possible to analyze accurately a mixture of deuterated hydrocarbons without the mass spectral patterns for the individual components, and the preparation of all the deuterated isobutanes was not undertaken. It is possible, however, to obtain semiquantitative information from the mass spectral data in terms of the number of deuterium atoms in the molecule without regard to their specific positions. Even such calculations involve some estimations concerning sensitivities and fragmentation patterns.

When the extent of exchange exceeded 10%, the parent mass peaks were used to calculate the distribution of the various polydeuterated isobutanes. For such calculation, the relationship of the parent peaks to fragment peaks was derived from those of isobutane. A check on the over-all % exchange is afforded by use of C_3^+ fragment peaks. In this case, the total C_3^+ fragmentation is summed up, and the amount of undeuterated isobutane is calculated from the corrected mass 57 peak, to which the deuterated species contribute only a small amount. When exchange is less than 10%, the propyl ion peaks are used for analysis. This latter method does not give individual deuterated species, but instead groups of deuterated species—for example, depending on the distribution of the D atoms, a trideuterated compound would show C_3^+ fragmentation up to mass 46.[5]

It is difficult to prepare batches of deuterated catalyst that will be exact duplicates insofar as exchange activity is concerned. This is probably due to variations in the drying rates and in the manner in which the dried catalyst is rewetted. Thus, duplicate experiments with different batches of catalyst have varied by a factor of almost 2; with the same batch, repeat determinations are of the order of ±15% of the amount reported. Therefore, in this report all exchange data relating to the effect of a given variable were determined on the same preparation of deuterated catalyst.

The experimental data are shown in Tables I to III and in Figs. 1 and 2.

TABLE I

HYDROGEN EXCHANGE BETWEEN CATALYST AND THE BUTANES; EFFECT OF STRUCTURE OF THE BUTANE AND POSITION OF THE HYDROGEN

Hydrocarbon	Catalyst form	Exchange, % 1 hour	4 hours
n-Butane	D	1	
Isobutane	D	34	
2-Methylpropane-1-*d*	H	20	49
2-Methylpropane-2-*d*	H	2	3

Conditions.—Exchange experiments at 150° for times given above using 3.5 g. of catalyst and 11.2 cc. (S.T.P.) of butane. The catalyst, calcined at 730° during manufacture, was converted to H or D form by addition of H_2O or D_2O at 28° and then dried again under vacuum at 315°. For experiments in which the catalyst was dehydrated at 525°, exchange was less than 1% in all above examples.

TABLE II

EXCHANGE BETWEEN ISOPENTANE AND 2-METHYLPROPANE-2-*d* IN THE PRESENCE OF CRACKING CATALYST

Reaction at 150° for 1 hour; original reaction mixture, 55.7% 2-methylpropane-2-*d*, 44.3% isopentane; *x* means that the location of the deuterium is uncertain.

Reaction Product, %	
No olefin added	2% isobutene added
31 i-C$_4$	30 i-C$_4$
42 i-C$_4$, 2-*d*	45 i-C$_4$, 2-*d*
2 i-C$_4$, x-d_2	1 i-C$_4$, x-d_2
8 i-C$_5$	8 i-C$_5$
16 i-C$_5$, x-d_1	15 i-C$_5$, x-d_1
1 i-C$_5$, x-d_2	1 i-C$_5$, x-d_2
	No olefin found

TABLE III

EXCHANGE BETWEEN DEUTERATED CATALYST AND ISOBUTANE IN THE PRESENCE OF ADDED AIR AND OLEFIN[b]

Catalyst drying temp., °C.	Olefin added,[a] %	Air added,[a] %	Exchange, %
315	0.3	0	34
370	.3	0	19
425	.3	0	7
525	.3	0	2
525	.0	0	2
	.1	0	2
	.3	0	3
	1.0	0	7
	3.0	0	14
525	0.0	1.0	3
	.0	10.0	5
525	.3	10.0	5
	3.0	10.0	14

[a] Based on volume of isobutane. [b] Reaction conditions were as in Table I except that the air or olefin was added just before addition of the isobutane.

Discussion

Several important facts are evident from the data. Referring to Table I, it is seen that at 150° extensive hydrogen exchange occurs between catalyst and isobutane, while under the same conditions the exchange with normal butane is lower by more

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[5] Paper by J. Terrell presented before the Eastern Regional Meeting of the Mass Spectrometer Group at Wilmington, Delaware, September, 1950.

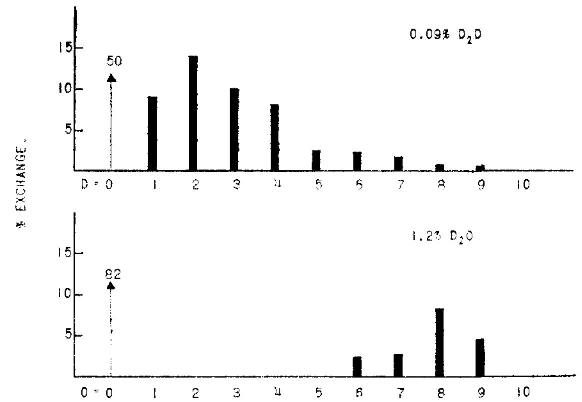

Fig. 1.—Typical distributions of deuterated isobutanes in product: catalyst dried at 525° and D_2O added back in amounts shown.

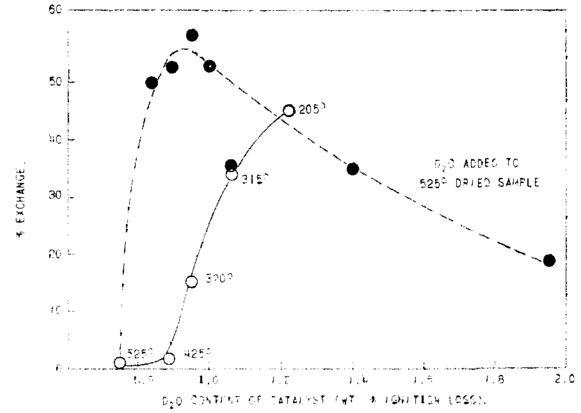

Fig. 2.—Exchange at 150° for 1 hour between deuterated catalyst and isobutane as a function of D_2O content of the catalyst: ○, catalyst samples pretreated by drying under vacuum at the temperatures given or ●, by drying at 525° and adding back D_2O.

than an order of magnitude. It is noteworthy that polydeuterated isobutanes are found in amounts far greater than would be expected from a statistical distribution of deuterium in the hydrocarbon, as seen in Fig. 1. Moreover, in the isobutane molecule, although the hydrogen atoms attached to primary carbon atoms exchange rapidly, the hydrogen attached to the tertiary carbon atom exchanges with the catalyst very slowly, if at all. The small exchange observed may arise from a possible small amount of isobutyl halide in the *t*-butyl halide used in the preparation of the 2-methylpropane-2-*d*. The hydrogen attached to a tertiary carbon does exchange with hydrogen of another isoparaffin. In view of the fact that such exchange, shown in Table II, gives rise primarily to a monodeuterated isopentane, and in view of the general lack of exchange reactivity of this tertiary hydrogen with the catalyst, it is believed that this exchange occurs with the tertiary hydrogen of the second isoparaffin molecule. The increase in the C_4:C_5 ratio in the product gas relative to that charged is due to the greater sorption of the heavier hydrocarbon by the catalyst with subsequent fractionation of the gas sample taken off. Cracking of these paraffins does not occur to a measurable extent under the conditions used for the exchange study.

The addition of air or of olefin to the isobutane–catalyst system accelerates the exchange reaction only to a relatively minor extent. On the contrary, the effect of the water content of the catalyst is critical. As shown in Fig. 2, by drying to higher temperatures the ability of the catalyst to catalyze exchange is almost eliminated, even though the catalyst in all cases contains an appreciable "water" content. By "water" content of the catalyst is meant the amount of water which can be driven off at sintering temperatures, about 1000°, and does not imply that water as such is present in the catalyst. After calcination, the water present in a catalyst is probably there as OH in AlOH and SiOH. Such attached water has been termed "constitutional."

Even more important than the absolute level of water content is the effect of adding back very small amounts of water to the dehydrated catalyst. For example, if the catalyst is dried at 525° and water added back to a moisture content equivalent to drying at 425°, the catalyst is far more active than one dried at 425° only (see Fig. 2). A series of experiments was also performed in which the catalyst was first calcined at 650° and water added back, with similar results.

Upon exchange it is also found that the distribution of deuterated species varies with the amount of water added. Not only does the water added back exchange, but, as may be calculated from the data, other hydroxyl of the structure, previously inactive for exchange, becomes activated. This was particularly evident in a special experiment in which 0.05% H_2O instead of D_2O was added back to the deuterated sample dried at 525° with the result that in this case deuterium appeared in the isobutane and 16% of the butanes was found to contain deuterium. A similar result was found with a deuterated catalyst dried at 650° and rewetted with H_2O. This must mean that "water" in a catalyst is present in more than one structural arrangement. It has been previously shown that extensive reactions occur between water and catalyst.[6] After dehydration, when water is added back to the catalyst, such water is involved in the constitution of "active sites" and labilizes other hydrogen atoms present in the catalyst structure. The manner in which this water may take part in the exchange reaction has been outlined by Milliken, Mills and Oblad.[2] Here the water is playing the same role as water, hydrogen halides and other co-catalysts play in aluminum halide and other "acid" catalyst systems.

To explain the observed exchange reactions, keeping the known properties of the catalyst in mind, three reaction steps are proposed for the isobutane exchange: (1) complex formation between catalyst and hydrocarbon; (2) exchange of hydrogen between catalyst and complex; (3) hydride ion transfer between isobutane and deuterated complex.

Step 1.—The reaction of an olefin with a potential Brönsted acid present in the catalyst structure is an easy means of forming a polarized complex (carbonium ion). However, the reaction of isobutane with a potential Lewis acid present in the cata-

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(6) G. A. Mills and S. G. Hindin, This Journal, **72**, 5549 (1950).

lyst structure is also capable of producing a polarized complex (carbonium ion). The formation of this complex involves a distorting of the tertiary hydrogen into a pseudo hydride ion. This should occur more readily with isobutane than with normal butane. The evidence here is consistent with this mechanism since the addition of olefin to carefully purified isobutane accelerates the exchange reaction only to a relatively minor extent. The amount of olefin introduced with the purified isobutane can only have been very small since there was used a small amount of hydrocarbon relative to catalyst. However, the possibility that the catalyst produces some olefin from isobutane cannot be ruled out completely.

Step 2.—The hydrogen exchange is visualized as occurring between the carbonium ion and catalyst surface through proton interchange. It is significant that for a small extent of exchange there appear polydeuterated isobutane molecules in far greater abundance than is expected on a statistical basis. This means that Step 2 is fast relative to Step 3, so that the relatively few polarized complexes are highly deuterated and, therefore, become highly deuterated isobutane molecules when Step 3 occurs. However, on long times of contact at elevated temperature it was found (using methane) that the total hydrogen and deuterium of the catalyst and hydrocarbon come to statistical equilibrium.

The actual mechanism of Step 2 involves the mobility of hydrogen or of the hydrocarbon over the catalyst surface. It appears to us more likely that it is mobility of the hydrogen which is involved. The decrease in "water" content of the catalyst in going from 1.0 to 0.7% H_2O drastically reduces its ability to promote exchange. This must mean that the "water" lost is associated with catalyst sites active in the exchange. The function of this critical "water" content may be to allow hydrogen mobility. When dried to the lower "water" content, the hydrogen remaining may exist largely as inactive SiOH. On the other hand, another function of the water may be to provide the protons necessary for carbonium ion formation with olefin.[2] If "water" in the catalyst provides hydrogen mobility, then, even when no exchange is observed with catalyst dried at 525° there still may be exchange occurring with a very limited amount of hydrogen located at active sites on the catalyst.

Hydrogen attached to the tertiary carbon in isobutane exchanges only slowly, if at all, with the catalyst. This hydrogen is relatively negative and cannot exchange with the proton contained in the catalyst. However, there does occur an exchange with hydrogen held to tertiary carbons in other molecules by the mechanism of Step 3.

Step 3.—The transfer of a hydride ion from adsorbed isobutane to the deuterated carbonium ion provides for release by the catalyst of a deuterated isobutane. The hydrogen attached to the tertiary carbon atom in isobutane is most negative and it, therefore, should be removed most easily as a hydride ion. The observed difference in behavior between hydrogens attached to primary and secondary carbon atoms and the observed interchange of hydrogen between tertiary positions are consistent with this concept. Alternatively, if isobutane is held as a polarized complex by the Lewis acid of the catalyst, it may exchange and then be simply released.

The part played by the catalyst in Step 3 should be emphasized. The presence of potential Lewis acids in the catalyst may provide the driving force for loosening a hydride ion from the isobutane molecules with eventual transference of the hydride ion to the carbonium complex, itself a strong Lewis acid.

The similarity of the above reactions to other acid-catalyzed reactions is evident. The presence of a co-catalyst, hydrogen halides or water, or oxygen has been found necessary in aluminum halide catalysis.[7] The similarity to the exchange reactions between isobutane and sulfuric acid[8] is particularly striking.

It should be pointed out that the activity of a cracking catalyst for hydrogen exchange is not necessarily directly related to its cracking activity. For instance, of a silica, an alumina (Harshaw γ-Al_2O_3), and a silica-alumina, only the latter is active in catalytic cracking of petroleum. However, both the alumina and the silica-alumina were found to be active for hydrogen exchange with methane at <400°, whereas calcined silica gel was inactive even at 500°.

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[7] C. D. Wagner, O. Beeck, J. W. Otvos and D. P. Stevenson, *J. Chem. Phys.*, **17**, 419 (1949); H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 2518 (1946); A. G. Oblad and M. H. Gorin, *Ind. Eng. Chem.*, **38**, 822 (1946).

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