

Similarities and Differences in Activation of Small Alkanes by Liquid and Solid Strong Acids: An NMR, MS, and UV Spectroscopic Study

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The regioselectivity of H/D exchange occurring between isobutane and strong solid acids such as D₂O exchanged sulfated zirconia and acidic zeolites has been reinvestigated with increasing contact times on D₂O-exchanged USY zeolite and the results compared with those obtained by using 98% D₂SO₄. As expected, during the initial stage, both on the solid and in the liquid acid only the primary hydrogens of isobutane were exchanged for deuterons. However, with aging catalysts, deuterium is slowly introduced also in the tertiary position of isobutane, by a mechanism related to the formation of polyenylic ions which could be monitored by UV spectroscopy. When the catalyst is repeatedly replaced by fresh material, isobutane can be completely selectively deuterated on the primary position with both acids. The MS and NMR spectra show however that the isotopologs distribution in partially deuterated isobutane is very different when D₂SO₄ is used in comparison with the solid acid.

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INTRODUCTION

Acid-catalyzed transformation of hydrocarbons, such as cracking, isomerization and alkylation, are of future importance in the petrochemical industry (1, 2). For the understanding of these reactions there is however a strong contrast between the general agreement on the role of carbocations as reaction intermediates and the lack of information over their mode of formation. In the presence of liquid superacids (3), alkanes behave as σ -bases (4) and the protolytic activation reaction (5) can be quantitatively followed by trapping the resulting cations with carbon monoxide (6). On solid acids, despite a general agreement on the carbocationic nature of the reaction intermediates, the alkane activation step leading to the first carbenium ion is still one of the major unanswered questions (7). On strong solid acids such as acidic zeolites, heteropolyacids or sulfated zirconia, regioselective H/D exchange, which is observed when small alkanes are contacted at 100–150°C with D₂O exchanged solids (8), indicates that alkenes are generated as reaction intermediates from the carbocations on the surface. This reaction sequence is very similar to that suggested in the early fifties for isoalkanes contacted with D₂SO₄ at room

temperature (9). Considering the research efforts, devoted presently to understand and control alkane activation and functionalization (10), we have reinvestigated the H/D exchange occurring between D₂SO₄ and isobutane at room temperature and for comparison with a D₂O-exchanged solid acid, here H-USY. We present here our results based on ¹H, ²H-NMR, MS and UV spectroscopy which underline the similarities and differences between solid acid and sulfuric acid-catalyzed isobutane activation.

EXPERIMENTAL

Catalysts

D-USY. As catalyst we used a D₂O-exchanged acidic steam dealuminated zeolite USY (framework Si/Al = 4.5, residual Na₂O = 0.5% weight) (11). The zeolite was pretreated with dry nitrogen (38 mL/min) at 500°C for 30 min. Deuteration was then carried out with 3 mol% D₂O in N₂ at 250°C for 60 min followed by a N₂ purge of 15 min. D₂SO₄, 98% weight, 99.9% isotopic purity from Aldrich Chemicals was used without further purification. Isobutane was purchased from Alphagaz Isobutane N35 and checked for purity by GC, no isobutene could be detected.

Apparatus and Procedure

Zeolite catalyzed H/D exchange. The catalytic reaction was run in an all glass, grease free, flow system (12). About 12 g of HUSY was pretreated with dry nitrogen (38 mL min⁻¹) at 500°C for 30 min. Deuteration was then carried out with 3 mol% D₂O in N₂ at 200°C for 1 h, followed by a N₂ purge of 30 min. The temperature was reduced to 100°C and isobutane (100 mL, 4.46 mmol, ca. 6 mol% in N₂) was passed at a rate of 20 mL min⁻¹ over the catalyst. After reaction, isobutane was condensed in a cold trap and stored at -78°C for the next pass whereas the catalyst was flushed with N₂, reactivated at 500°C for 1 h, and again exchanged with D₂O at 200°C. After each pass isobutane was analyzed by GC-MS for D content. This cycle was repeated several times for isotopic enrichment of isobutane.

D₂SO₄ catalyzed H/D exchange. The catalytic reaction was also run in an all-glass grease free set-up with a recirculation pump. Isobutane (25 mL, 1.1 mmol) was bubbled at a rate of 4 mL min⁻¹ through 5 mL, 93.5 mmol, 98% D₂SO₄ (99.9% D), and recirculated at room temperature during various length of time from 2 to 20 h. At the end of each period isobutane was condensed in a cold trap. Qualitative and quantitative analysis of deuterium content and distribution in isobutane was obtained by GC-MS and by comparison of the ¹H and ²H-NMR spectra.

Mass spectrometry. MS analysis was performed on a Carlo Erba QMD-1000 spectrometer with a JSW Scientific DB 624 column ($\phi = 0.25$ mm; film, 1.4 μ m, $l = 30$ m).

NMR. The spectra were recorded on a Bruker AM400 MHz spectrometer. For ¹H and ²H measurements a CF₂Cl CFCl₂ solution of a CDCl₃/CHCl₃ mixture was used as an internal standard.

Gas chromatography. A Hewlett Packard 5840 Series II with a HP5 capillary column (30 m) was used for hydrocarbon analysis.

RESULTS AND DISCUSSION

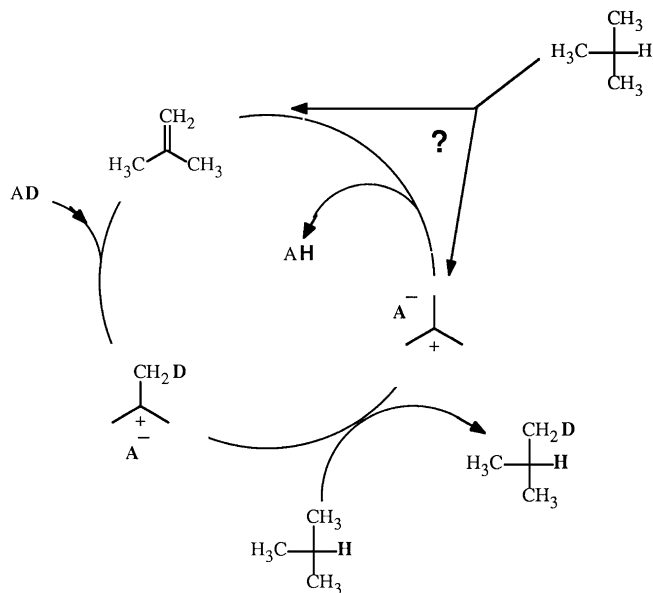
Isobutane is a convenient model for alkane activation studies as, even under superacidic conditions, it leads to very simple product distribution based on the higher reactivity of its tertiary C–H bond (13). Whereas in DF–SbF₅ the reversible protonation of the alkane occurs on all C–H bonds, we have shown in the recent years (8) that on deuterated solid acids only the primary protons of isobutane could be exchanged for deuterons, a rule which was verified for all branched small alkanes and a large variety of D₂O exchanged solid acids including SZ, H-ZSM5, HBEA, HUSY, H-EMT, H-MAZZ, and heteropolyacids. The catalytic cycle, rationalizing this regiospecific exchange, is shown in Scheme 1.

In accord with this scheme, based on Markovnikov's rule (14) and Stevenson's experiments in the early fifties (9), no deuterium should be found in the tertiary position as only "D⁺" is present in the reaction system.

For this reason, when we tried to prepare 100% non-deutero-2-methyl-2-H-propane by this deuteration technique, using D₂O-exchanged HUSY, we were surprised to notice that deuterium was appearing in the tertiary position when after a series of deuteration, reactivation cycles, more than 90% of the protons were exchanged for deuterium. The introduction of a deuterium in the tertiary position could be rationalized by any one of the following ways:

(i) a minor competitive pathway such as direct electrophilic substitution on the tertiary C–H bond as it occurs in liquid superacids;

(ii) a slow D-scrambling in *t*-butyl ion via the thermodynamically unfavorable primary isobutyl cation (Scheme 2);



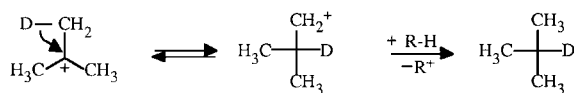
SCHEME 1. Catalytic cycle of H/D exchange on solid acids.

(iii) a different mechanism associated with the formation of higher molecular weight material on aging catalyst.

In contrast with isobutane which can only transfer a tertiary hydride to the *t*-butyl ion, deuterated alkenes and especially polyenes can easily transfer an α -deuteride to the carbenium ion in a process which generates alkenylic and polyenylic ions.

These ions, which can be easily obtained by protonation of the corresponding dienes and polyenes, are known to be stable in concentrated sulfuric acid in which they could be observed as long-lived species by NMR and UV spectroscopy (15). That alkenyl cations are also formed on sulfated zirconia has been suggested by Védrine and co-workers who observed a strong UV absorption band at 292 nm (16). More recently Knözinger and co-workers were able by UV diffuse reflectance spectroscopy to follow the formation of these alkenyl and polyenyl ions during the reaction of *n*-butane on SZ in the absence of hydrogen as well as the disappearance of the corresponding UV bands when the catalyst was regenerated under O₂ above 500°C (17). Cycloalkenyl ions are also sufficiently stable in zeolite environment to allow their direct observation by solid state NMR (18).

For this reason we have reinvestigated the H/D exchange reaction occurring at room temperature between isobutane and D₂SO₄ already reported in the early fifties by Stevenson *et al.* (9). One mmol isobutane was recirculated at room



SCHEME 2. Intramolecular D-scrambling in *t*-butyl ion.

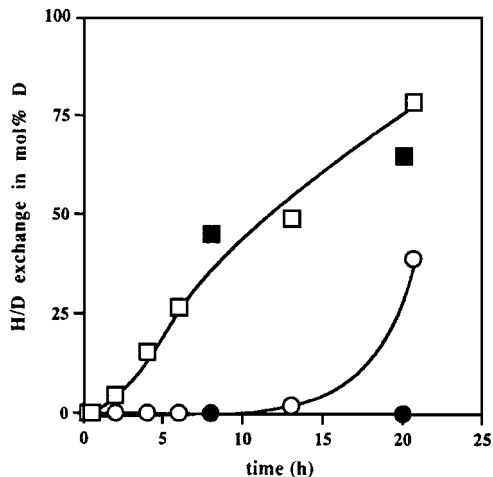
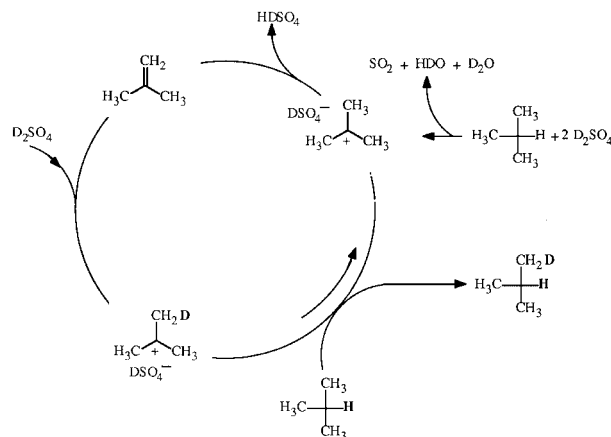
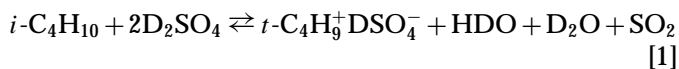


FIG. 1. Regioselectivity of H/D exchange vs time of recirculation of isobutane in D_2SO_4 . (□) Primary and (○) tertiary hydrogens. (■, ●) Same but renewing the catalyst every 4 h.

temperature through 5 mL D_2SO_4 and the amount of deuterium introduced in the alkane versus time on stream was controlled by $^1H/^2H$ NMR. (In contrast with zeolitic material that contains often less than 1 meq acid site per gram, D_2SO_4 has as much as 20 meq D g^{-1} allowing larger isotopic enrichment of isobutane before impoverishment of the catalyst). The results are shown in Fig. 1.

During the first 30 min only SO_2 (m/z 64) was detected besides undeuterated isobutane C_4H_{10} . During this induction period the t -butyl cations are generated by oxidation of the alkane by sulfuric acid following reaction [1]:



SCHEME 3. Catalytic cycle of H/D exchange in D_2SO_4 .

As expected, after this induction period isobutane is increasingly deuterated in the primary position following Scheme 3.

We noticed that after 13 h recirculation, when already 50% of the primary hydrogens were exchanged for deuterium, a small amount of D (0.7 at.%) appeared also in the tertiary position. When the acid was used for a longer period (20 h) we found as much as 39 at.% D in the tertiary position compared with 79 at.% in the primary position. Clearly the exchange was no more completely regioselective. As, during the reaction, the acid turned slightly yellow we repeated the same experiment but replacing the acid by fresh D_2SO_4 every 4 h. In this case after 20 h of recirculation no deuterium was found in the tertiary position, whereas in the primary an isotopic enrichment of 65% was reached. For this reason it was easy to assign the change in regioselectivity to aging of the acid solution and we investigated

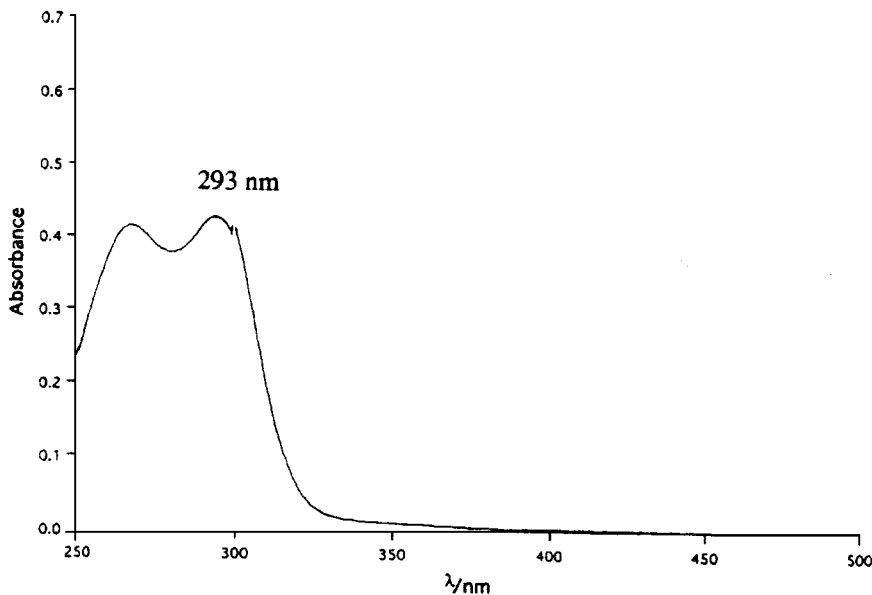


FIG. 2. UV spectra of H_2SO_4 solution after 1 h recirculation of isobutane.

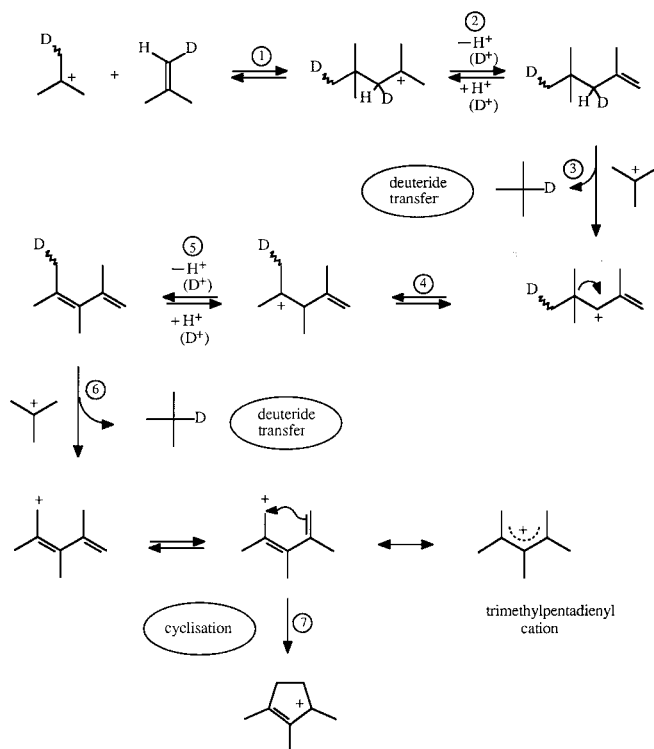
the acid by UV visible spectroscopy. Figure 2 shows the UV spectrum of the D_2SO_4 solution after 1 h on stream.

A strong broad band appears at 290 nm, a region which has been assigned earlier to substituted cyclopentenyl cations (15).

On the basis of our H/D exchange experiments we know that the *t*-butyl ion is in equilibrium with isobutene under our reaction conditions. It is thus easy to rationalize the formation of this type of ions from isobutane by a series of alkylation (step 1), deprotonation (steps 2 and 5), hydride (or deuteride) transfer (steps 3 and 6), methyl migration (step 4), and cyclization reactions (step 7) as described in Scheme 4.

Reactions of this type are known to occur in H_2SO_4 , when dienes and polyenes are used as starting materials. The reaction sequence described in this scheme does not proceed in superacid media (3), in which alkenes cannot be formed as the conjugate bases are too weak to allow deprotonation of the *t*-butyl cation.

In the course of these reactions, once the *t*-butyl ion is partly deuterated, deuterated alkenes and polyenes will slowly be formed and the hydride (deuteride) transfer (steps 3 and 6 in Scheme 4) can introduce deuterium on the tertiary carbon. This will only be noticed after longer times on stream when polyenyl cations are formed in larger quantities either in D_2SO_4 or on the surface of the solid D_2O -exchanged acid. These cycloalkenyl ions which are the precursors of aromatics are in fact the precursors of coke formation. Scheme 5 describes the formation of aromatics from the cyclopentenyl ions by consecutive hydride shift (step 1), ring enlargement via protonated cyclopropane (steps 2 and 3), deprotonation (step 4), hydride or deuteride



SCHEME 4. Formation of cycloalkenyl ions from isobutane with concomitant deuteride transfers.

transfer (step 5), aromatization (step 6) and alkylation reactions.

The formation of polyenylic and aromatic ions during the reaction of isobutane in sulfuric acid can be followed by UV visible spectroscopy as the change in the absorption

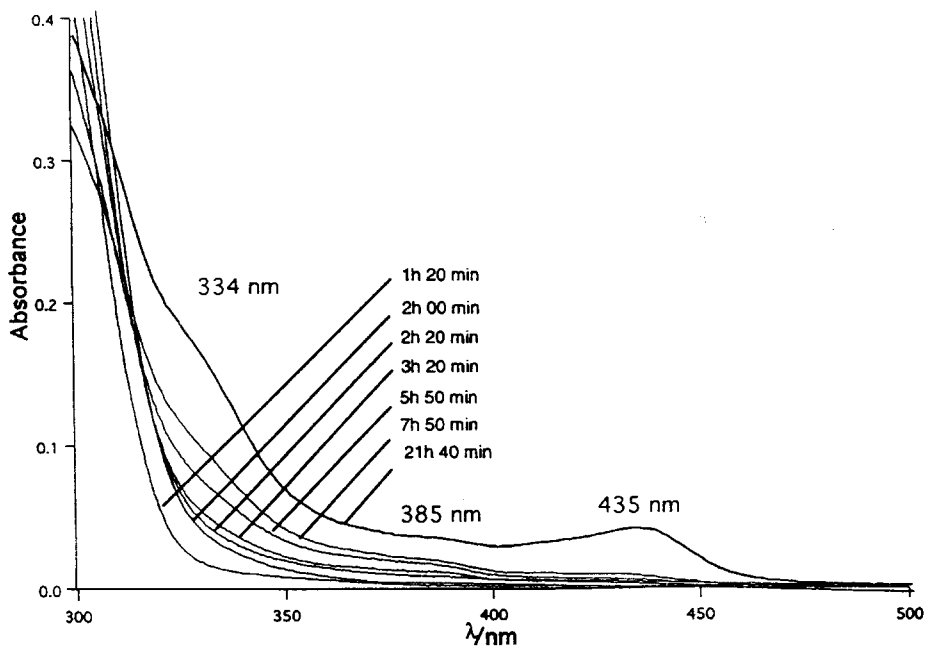


FIG. 3. Variation of UV visible absorption bands vs recirculation time.

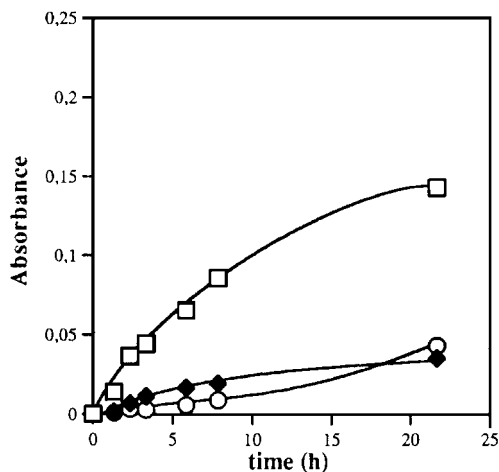
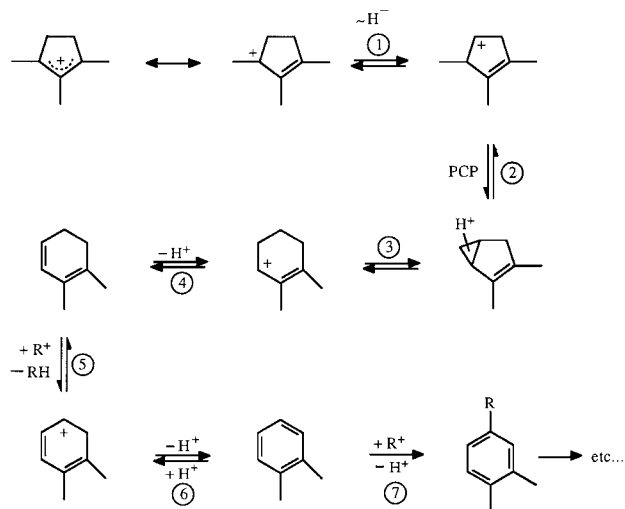


FIG. 4. Change in intensity of the absorption bands vs time of recirculation. □, 334 nm; ◆, 385 nm; ○, 435 nm.

spectra shows the increasing appearance of bands in the higher wavelength region (Fig. 3) known to be representative of more delocalised polyenyl and phenylsubstituted alkenyl cations (15).



SCHEME 5. Formation of aromatic systems from cycloalkenyl ions.

Figure 4 shows the time dependence of the 3 UV bands at $\lambda_{\max} \sim 334, 385,$ and 435 in accord with the increasing formation of heavier and more delocalized aromatic polyenyl cations.

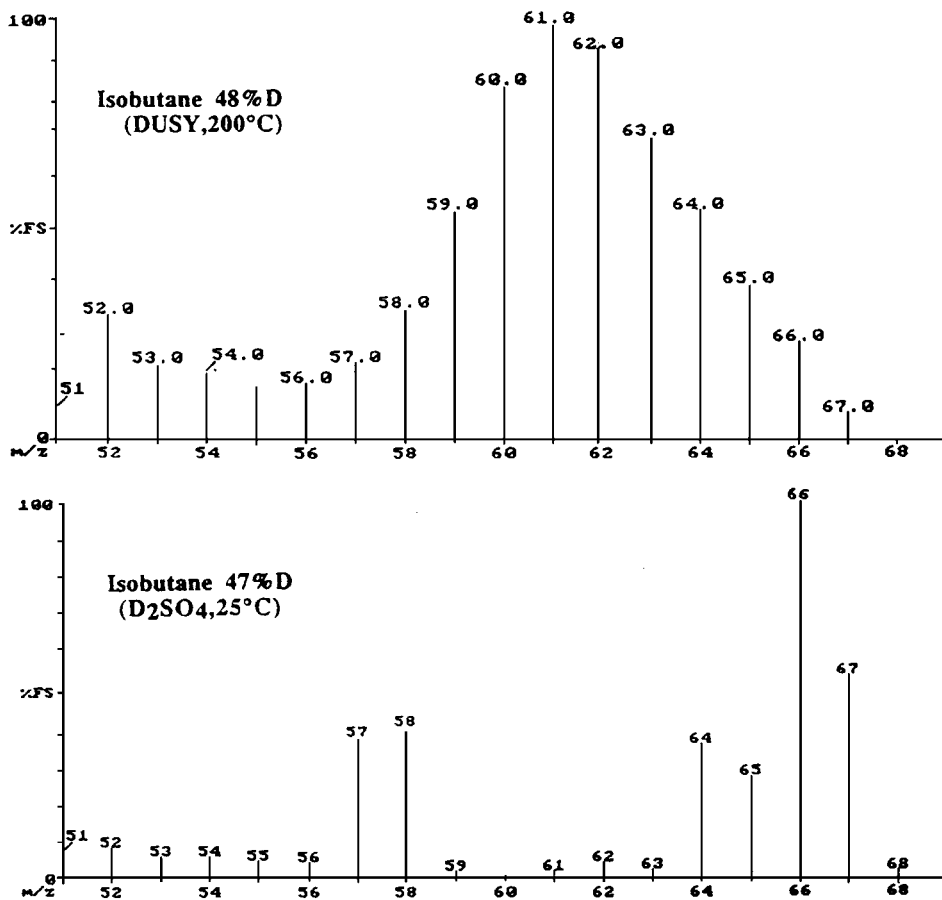


FIG. 5. MS spectra of isobutane deuterated with liquid and solid acid.

Comparison of these wavelength with those observed by Knözinger on the solid indicates that the ions formed on the solid from *n*-butane have analogous chromophores but that the structure is not exactly the same as when isobutane is the starting material. This is not surprising as a strong dependence of λ_{\max} on small structural differences has been noticed by Deno and co-workers (15a).

It is understandable that, in the experiments with the solid D₂O-exchanged catalyst, which has been reactivated at 500°C several times (see experimental part), deuterium appears in the tertiary position much later than in the experiments performed with D₂SO₄.

Comparison of the Isotopolog Distribution

During the deuteration reaction both by solid and liquid acids, we monitored the introduction of deuterium in isobutane by GC-MS in order to check the absence of decadeutero alkane. We noticed that the isotopolog distribution was very different, depending on the catalyst:

—with the solid acid: isobutane was deuterated statistically during recirculation with a Gaussian curve which

shifted progressively from the small d_1 - d_3 m/z values to the larger d_7 - d_9 values as the D content increased.

—with the liquid acid in contrast, the mass spectra of isobutane deuterated by D₂SO₄ showed the permanent coexistence of d_0 and increasing d_8 - d_9 isotopologs with little participation of intermediate d_1 - d_7 isotopologs. Figure 5 shows the mass spectra of approximately 50% deuterated isobutane obtained after sufficient contact time with either the liquid or the solid acid.

This difference in isotopolog distribution is also clearly apparent in the ¹H NMR spectra (Fig. 6) showing the coexistence of a large amount of unlabelled isobutane and largely deuterated isobutane (with methine and methyl hydrogens shifted upfield by isotope effect on δ).

The origin of this difference in isotopolog distribution must be based on differences in rate of hydride transfer between the incoming alkane and the deuterated carbenium ions.

The results seem to indicate that in D₂SO₄ the deprotonation/reprotonation equilibrium between the *t*-butyl ion and isobutene is very fast in comparison with the hydride transfer step as, even when 50% of deuterium has entered in

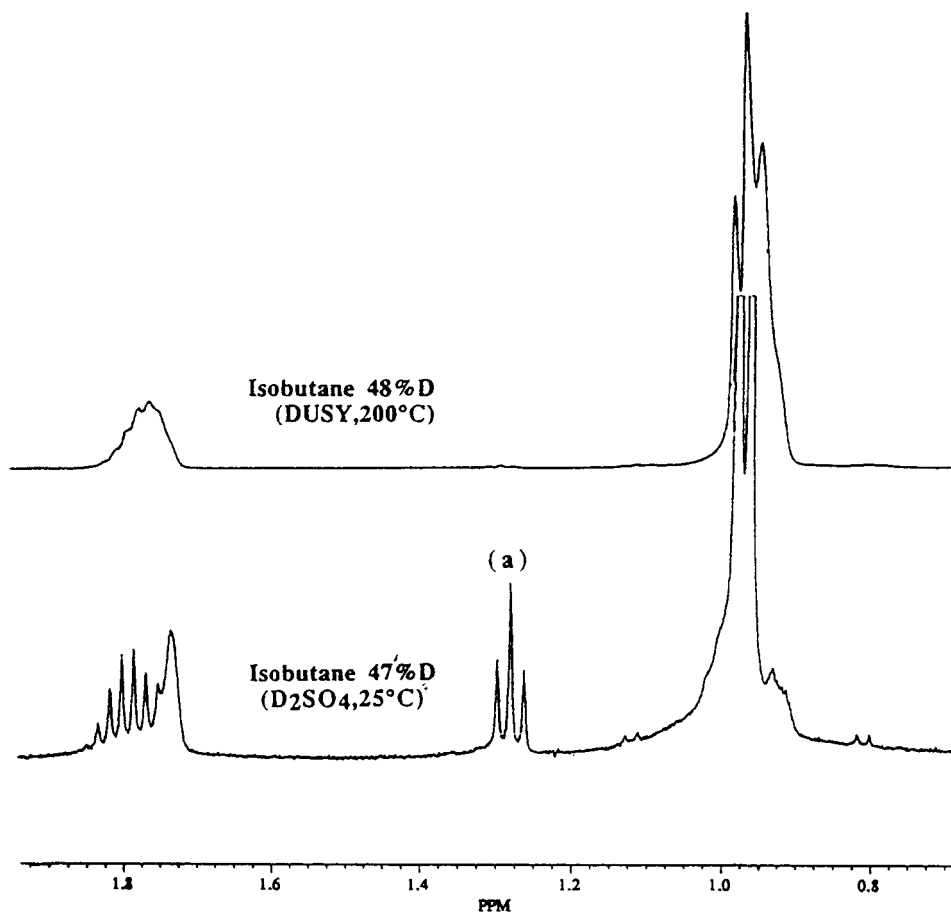


FIG. 6. ¹H NMR spectra of isobutane deuterated with liquid and solid acid.

the alkane, a large part of isobutane has not been involved. This could be assigned to the fact that, in each bubble, the reaction only takes place at the interface and thus a large part of isobutane (even after 15 h recirculation time) leaves the reactor unreacted. On the other hand, if we assume that the ionization and hydride transfer steps take place in the liquid acid phase we should ascribe this result to the low solubility of isobutane in D_2SO_4 . For this reason, with ionized isobutane, the catalytic cycle (Scheme 3) will be covered several times before hydride transfer occurs. On the solid, however, the contact between the alkane and the adsorbed carbenium ions seems more homogeneous as a statistical distribution is observed at all deuterium enrichment levels. The alkyl carbenium ion must first desorb as an alkene before meeting the next O-D site, which is less favorable at 423 K than undergoing a hydride transfer from passing isobutane.

The initial step of isobutane activation on the solid acid leading to the *t*-butyl ion or alkoxy type intermediate is however unsolved. During the formation of the reaction intermediates, *t*-butyl ion participating in the catalytic cycle, HD should be produced if the activation proceeds protolytically. However, as the number of sites participating in the activation step is not known it is not sure that an equivalent amount (2.7×10^{-3} eq · H_2/g of catalyst) should be expected. We have up to now not been able to detect hydrogen by GC. But research in this direction is under progress.

CONCLUSION

The H/D exchange occurring between isobutane and D_2O -exchanged USY at 150°C shows that the completely regioselective exchange of the primary protons for deuterons takes place only on the fresh catalyst, as long as no polyenylic material has built up. In D_2SO_4 the H/D exchange is preceded by an induction period during which the alkane is oxidized with formation of the *t*-butyl ion and SO_2 . The H/D exchange thus takes place very similarly in the liquid and on the solid acid, involving the deprotonation of the *t*-butyl carbenium ion and deuteration of isobutene. With time on stream, alkylation, oligomerization, and aromatization reactions produce higher molecular weight polyenylic material. These polymers capable to transfer deuteride to the carbenium ions lead also to a slow deactivation of the

catalysts. However, considering that the oxidative activation of the isoalkane by H_2SO_4 is proven, the question of the initial step of carbocation formation from the alkane on solid acids is however still unanswered.

REFERENCES

1. Pines, H., in "The Chemistry of Catalytic Hydrocarbon Conversion." Academic Press, New York, 1981.
2. Olah, G. A., and Molnar, A., in "Hydrocarbon Chemistry." Wiley, New York, 1995.
3. Olah, G. A., Prakash, S., and Sommer, J., in "Superacids." Wiley, New York, 1985.
4. Olah, G. A., *Angew. Chem., Int. Ed. Engl.* **12**, 173 (1973).
5. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., *J. Am. Chem. Soc.* **93**, 1251 (1971).
6. (a) Sommer, J., and Bukala, J., *Acc. Chem. Res.* **26**, 370 (1993); (b) Sommer, J., Bukala, J., and Hachoumy, M., *Res. Chem. Intermed.* **8**, 753 (1996); (c) Sommer, J., Bukala, J., Hachoumy, M., and Jost, R., *J. Am. Chem. Soc.* **119**, 3274 (1997).
7. (a) Corma, A., *Chem. Rev.* **95**, 559 (1995); (b) Sommer, J., Hachoumy, M., and Jost, R., *Catal. Today*. [in press]
8. (a) Sommer, J., Hachoumy, M., Garin, F., and Barthomeuf, J., *J. Am. Chem. Soc.* **116**, 5491 (1994); (b) Sommer, J., Hachoumy, M., Garin, F., Barthomeuf, J., and Vedrine, J., *J. Am. Chem. Soc.* **117**, 1135 (1995); (c) Sommer, J., Habermacher, D., Hachoumy, M., Jost, R., and Reynaud, A., *Appl. Catal. A: Gen.* **146**, 193 (1996).
9. (a) Otvos, J. W., Stevenson, D. P., Wagner, C. D., and Beek, O., *J. Am. Chem. Soc.* **73**, 5742 (1951); (b) Stevenson, D. P., Wagner, C. D., Beek, O., and Otvos, J. W., *J. Am. Chem. Soc.* **74**, 3269 (1952).
10. (a) Hill, C. L., in "Activation and Functionalization of Alkanes." Wiley, New York, 1989; (b) Sommer, J., Special Issue on C_2 - C_5 alkane activation, *Appl. Catal. A, Gen.* **146** (1996).
11. Mirodatos, C., and Barthomeuf, D., *J. Catal.* **114**, 121 (1988).
12. O'Conneide, A., and Gault, F., *J. Catal.* **37**, 311 (1975).
13. (a) Culmann, J.-C., and Sommer, J., *J. Am. Chem. Soc.* **112**, 4057 (1990); (b) Sommer, J., Bukala, J., Rouba, S., Graff, R., and Ahlberg, P., *J. Am. Chem. Soc.* **114**, 5884 (1992).
14. Markovnikov, V. (1838-1904). Born in Russia, Moscow University.
15. (a) Deno, N. C., Richey, H. G., Friedman, N., Hodge, J. D., Houser, J. J., and Pittman, J. J., *J. Am. Chem. Soc.* **85**, 2991 (1963); (b) Soerensen, T. S., *J. Am. Chem. Soc.* **87**, 5075 (1965); (c) Deno, N. C., in "Carbonium Ions" (G. A. Olah and P. v. R. Schleyer, Eds.), Vol. II, p. 783. Wiley, New York, 1970; (d) Soerensen, T. S., in "Carbonium Ions" (G. A. Olah and P. v. R. Schleyer, Eds.), Vol. II, p. 807. Wiley, New York, 1970.
16. Chen, F. R., Coudurier, G., Joly, J. F., and Védrine, J. C., *J. Catal.* **143**, 616 (1993).
17. Spielbauer, D., Mekhemer, G. A. H., Zaki, M. I., and Knözinger, H., *Catal. Lett.* **40**, 71 (1996).
18. Haw, J. F., Nicholas, J. B., Xu, T., Beck, L. W., and Ferguson, D. B., *Acc. Chem. Res.* **29**, 259 (1996).