2. The heats of wetting of the hydrated amorphous silica surface by normal aliphatic alcohols and hydrocarbons are independent of the number of carbon atoms in the molecules and are 220 and 65 mJ/m², respectively.

3. The interphase (liquid-solid) surface layer or normal alcohol molecules on silica gel is a Langmuir palisade with the OH alcohol groups directed toward the silica surface.

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ISOMERIZATION OF BUTANE CATALYZED BY CH₃COX·2A1X₃

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The isomerization of butane and isobutane by the action of acid catalysts involves the formation of the n-butyl cation, its rearrangement to the tert-butyl cation, and the reaction of the latter with butane, leading to isobutane and the regeneration of the n-butyl cation:

 $\mathrm{CH_{3}CH_{2}CH_{3}} \xrightarrow{\oplus} \mathrm{CH_{3}CH} \xrightarrow{\oplus} \mathrm{CH_{2}CH_{3}} \xrightarrow{+ \underline{1, 2 - \mathrm{Me} \ \mathrm{shift}}} \xrightarrow{(\mathrm{CH_{3}})_{3} \overset{\oplus}{\mathrm{C}} \xrightarrow{\mathrm{n-C_{4}H_{9}}} (\mathrm{CH_{3}})_{3} \mathrm{CH} + \mathrm{CH_{3}^{\oplus}CHCH_{2}CH_{3}}$

The conversion of butane to isobutane is accompanied by the release of 8.53 kJ/mole [1]. Nevertheless, only strong Lewis acids are capable of producing this reaction [2]. Even promoted aluminum halides such as $HX-AlX_3$ (X = C1, Br) at 20°C produce this isomerization only very slowly (Table 1).

The use of high temperatures leads to an increase in the fraction of side reactions and the need to carry out this isomerization under thermodynamically less favorable conditions (the equilibrium mixture of butanes at 27°C contains 80% isobutane [1, 3], while it contains only 59% isobutane at 130°C [9]). Olah et al. [7] have shown that the new superacid TiOH_2^+ [B(OTf)₄]⁻ catalyzes the isomerization of butane at 20°C. However, this reaction is complicated by the formation of 2.7% methane, 6% ethane, 4% propane, and 2-methylbutane. The activity of this system is low and its stability is minimal; the reaction must be carried out under argon pressure.

In the present work, we studied the isomerization of butane at 20°C by the action of AcX· $2AlX_3$ systems (X = Br, Cl). We have recently shown that the AcBr·2AlBr₃ complex efficiently catalyzes the cracking of alkanes even at -10° C [11]. The major cracking product is isobutane (in addition to an oligomer with iso structure), and we had reason to assume that these systems would be good catalysts for the isomerization of butane under mild conditions.

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	T ., °C	Time, h	Isobutane yield			
Catalyst (Cat)			%	mole/ moleCat	selec- tivity	References
$\begin{array}{l} AlBr_{3} \\ HCl-AlBr_{3} \\ HCl-AlBr_{3} \\ HCl-AlCl_{3} \\ HCl-AlCl_{3} \\ SbF_{5}-SiO_{2} \\ SbF_{5}-TiO_{2} \\ SbF_{5}-SiO_{2}-Al_{2}O_{3} \\ SbF_{5}-SiO_{2}-Al_{2}O_{3} \\ TiOH_{2}^{\oplus}[B(OTf)_{4}]^{\oplus}* \\ Same \\ Promoted Pt catalyst \\ \end{array}$	27 80 100 20 20 20 20 20 20 20 20 20 20 20 20 170	$\begin{array}{c} 2000 \\ 4 \\ 12 \\ 18 \\ 64 \\ 280 \\ 280 \\ 20 \\ 280 \\ 24 \\ 48 \end{array}$	$\left \begin{array}{c} 78-82\\ 64\\ 63\\ 51\\ 21\\ 55\\ 59\\ 41\\ 48\\ 40\\ 57\\ 62\\ \end{array}\right $	16 5-6 20 0,3 0,5	97-98 94 73 71 82 71 84	$\begin{bmatrix} 3 \\ [4] \\ [5] \\ [4] \\ [6] \\ [6] \\ [6] \\ [6] \\ [6] \\ [7] \\ [7] \\ [8] \end{bmatrix}$

TABLE 1. Some Examples of the Isomerization of Butane by the Action of Acid Catalysts

 $\overline{* \text{Ti} = \text{CF}_3\text{SO}_2}$.

TABLE 2. Isomerization of Butane Catalyzed by $\rm AcBr\cdot 2AlBr_3$ and $\rm AcCl\cdot 2AlCl_3$ at 20°C

Catalyst	Time, h	C_4H_{10} : Cat	i-C4 in mixture, %	Isobutane yield,mole/ mole Cat	Selec- tivity
AcBr·2AlBr ₃ AcBr·2AlBr ₃ AcBr·2AlBr ₃ AcBr·2AlBr ₃ AcBr·2AlBr ₃ AcBr·AlBr ₃ AcCl·2AlCl ₃ AcCl·2AlCl ₃	$4,0 * \\ 6,5 * \\ 0,5 \\ 3.0 \\ 4,0 * \\ 3,0 \\ 7,5$	38:134:111:111:121:17:17:1	$ \begin{array}{c} 61 \\ 80 \\ 23 \\ 76 \\ 4 \\ 22 \\ 35 \\ \end{array} $	$20,9 \\ 24,3 \\ 2,5 \\ 8,4 \\ 0,8 \\ 1,5 \\ 2,5$	90 89 - - 100 97

* The reaction was carried out in liquid butane.

Indeed, we found that $AcX \cdot 2AlX_3$ compounds very efficiently isomerize butane at about 20°C both in the gas and liquid phases (Fig. 1).

Table 2 shows that in the presence of catalytic amounts of $AcBr \cdot 2AlBr_3$ at 20°C, the isobutane content in the butane mixture is close to the equilibrium value after only 3 h for $n-C_{u}H_{10}$: $AcBr \cdot 2AlBr_3$ equal to 11 and after 6.5 h in the case of a 34-fold excess of butane. The reaction selectivity is 90%. A study of the butane conversion products at maximal isomerization by the action of $AcBr \cdot 2AlBr_3$ showed that 6.8% 2-methylbutane is formed as a side product as well as butane acetylation products: 1.4% methyl isobutyl ketone and 0.3% mesityl oxide. All the yields are given relative to starting butane. Methane and butane were completely absent, while propane was present in only trace amounts.

The AcCl·2AlCl₃ is markedly inferior to the bromide system in its activity. However, it displays higher activity than some well-known acid catalysts (see Table 2). In contrast to AcBr·2AlBr₃, the classical Friedl-Crafts catalyst 1:1 AcBr·AlBr₃ has low activity at 20°C, the isobutane yield being only 4% after 4 h.

The reason for the unusually high catalytic activity of $AcX \cdot 2AlX_3$ complexes in the isomerization of butane (as in the case of other transformations of saturated hydrocarbons) may be the existence of ionic acetylium salts $CH_3CO^+Al_2Br_7^-$ and $CH_3CO^+Al_2Cl_7^-$ in solutions of $AcX \cdot 2AlX_3$ in apolar solvents [12]. In contrast, the 1:1 complexes in the same solutions do not contain acetylium ions, as shown in our laboratory by NMR spectroscopy.

It is also possible that the high reactivity of these systems is related to additional coordination of the acetylium cation with AlX_3 and formation of $[CH_3C=0 \leftarrow AlX_3]^+AlX_4^-$ complexes. In this case, we should assume that the concentration of such complexes is very low and beyond the limits of detection by NMR spectroscopy . However, regardless of the nature of the active species in $AcX \cdot 2AlX_3$ systems, we may conclude that these systems are superior to known aprotic superacid systems in the capacity to remove a hybride ion to form alkyl cations.



Fig. 1. Dependence of the yield of isobutane on time upon catalysis by AcX·2AlX₃ at 20°C: 1) AcBr·2AlBr₃, $n-C_4H_{10}$:AcBr·2AlBr₃ = 11:1; 2) AcCl· 2AlCl₃, $n-C_4H_{10}$:AcCl·2AlCl₃ = 7:1.

EXPERIMENTAL

Analytical-grade aluminum halides were used without further purification. A sample of dry, chromatographically pure butane was also employed. The acetyl halides were distilled in an argon atmosphere prior to use.

Isomerization of Butane in the Liquid Phase. The calculated amount of AcBr was added to a glass ampul containing a weighed sample of ground $AlBr_3$. After formation of the liquid AcBr·2AcBr₃ complex, excess butane was condensed into the ampul. The ampul was sealed, warmed to 20°C, and shaken vigorously for a given time. The ampul was then opened, and the gaseous products were analyzed. The remaining catalyst was hydrolyzed with aq. Na₂CO₃, and the products were extracted and analyzed by gas-liquid chromatography.

Isomerization in the Gas Phase. A weighed sample of ground AlBr₃ was introduced into a flask of known volume equipped with a device for taking gaseous samples, and the calculated amount of AcBr was added with stirring. After formation of the liquid AcBr·2AlBr₃ complex, the flask was evaporated and filled with butane. After a given time period, gaseous samples were taken with vigorous stirring and analyzed.

By analogy but in the presence of a twofold excess of CH_2Cl_2 (wt/wt), the isomerization was carried out by the action of AcCl·2AlCl₃.

The quantitative and qualitative gas-liquid chromatographic analyses of the gaseous products were carried out by the absolute calibration method on a Gazokhrom-3101 chromatography using a 7-m column packed with 15% dimethylsulfolane on Chromosorb P, and the liquids were analyzed on a Biokhrom-1 chromatograph with a 54 m \times 0.25 mm glass capillary column packed with XE-60 and methyl isopropyl ketone as the internal standard.

CONCLUSIONS

 $AcX \cdot 2AlX_3$ (X = Br, Cl) are efficient catalysts for the isomerization of butane at room temperature. The activity of these catalysts is superior to that of known catalytic systems.

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HEATS OF ADSORPTION AND CAPILLARY CONDENSATION

OF PENTANE ON SILICA GEL

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In a continuation of our study of the thermodynamics of capillary condensation [1], we carried out calorimetric measurements of the heats of adsorption of pentane on silica gel.

EXPERIMENTAL

The differential heats of adsorption were determined using a Tian-Calvet calorimeter. The adsorption was measured relative to the loss of liquid pentane in a calibrated capillary. The adsorption system did not contain greased valves.

A sample of pentane was purified by preparative chromatography. MSK commercial silica gel was additionally treated with acids, water vapor, and alkali. The specific surface of this sample was found by the BET method at different times on different instruments to fall in the range from 218 to 202 m²/g (we adopted $s_{BET}^{N_2} = 210 \text{ m}^2/\text{g}$). The total mesopore volume $V = 1.15 \text{ cm}^3/\text{g}$ and the mean diameter of an equivalent cylindrical pore d calculated using the formula d = 4V/s was found to be 22 nm. The maximum on the mesopore volume distribution curve relative to diameter, calculated from the adsorption isotherm and estimated by different methods, was found in the range from 14 to 20 nm (Fig. 1).

Prior to the experiments, the silica gel sample was heated at about 0.01 Pa to about 200°C. the heats of adsorption were measured at 20°C.

RESULTS AND DISCUSSION

Strictly speaking, the calculation of isosteric heats using the Clapeyron-Clausius equation in the hysteresis region is not entirely proper. However, the possible errors introduced by the irreversibility of the process are not great. The similar course for the change in the differential and isosteric heats depending on occupancy is evidence confirming these two curves (Fig. 2). After initial high heat values, they fall toward the end of the completion of the random monolayer (the BET monolayer volume a_m is 0.52 mmole/g) to about 30 kJ/mole and toward the end of the third monolayer, they become only about 1 kJ/mole greater than the heat of condensation. In the entire range for the sharp rise in the adsorption isotherm (from 2 to 9 mmoles/g), the heats remain equal to 28.2 kJ/mole.

In the region of the completion of adsorption (from 9 to 10 mmoles/g), the adsorption heats on both branches of the hysteresis loop display pronounced extrema due largely to the sharp change in the curvature of the meniscus and, as a consequence, sharp change in the Laplace pressure on the capillary condensed liquid.

The isosteric heats of adsorption are approximately 0.7RT greater than the differential heats. Theoretically, these discrepancies may reach the value of RT. The initial enhanced values (in the range of the monolayer) for the isosteric heats are also in good accord with the calorimetric measurements.

The thermodynamic calculation of the differential heats of capillary condensation on the basis of the adsorption data for the adsorption isotherm was plotted taking account of the temperature dependence of the molar volume v and surface tension σ of pentane according to our equation [2]

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