ACCELERATION OF THE REARRANGEMENT OF LONG-LIVED CARBOCATIONS ON ALUMINUM OXIDE SURFACES

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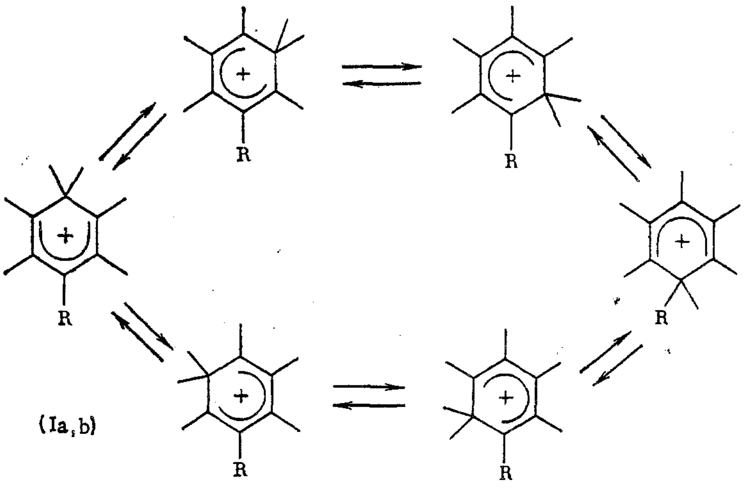
The rearrangement of carbocations or similar electron-deficient species is regarded as being a key step in the reactions of organic compounds on solid acidic catalysts [1-3]. Reactions of this type underlie many industrial processes, such as petroleum cracking, hydrocarbon isomerization, etc. [1-3]. However, the mechanisms of these reactions and the features of the reactivity of organic compounds on solid acidic catalysts remain largely unclear. Furthermore, the arguments supporting the "carbocation" hypothesis for such reactions on the basis of the similarity in the behavior of organic compounds on solid acid catalysts and in acid solution are not always obvious, particularly in view of the lack of direct experimental information on the influence of the solid catalyst surface on the rate of carbocation rearrangement (cf. [3, 4]).

In order to establish the features of carbocation rearrangements on a solid carrier as compared with a solution, we have examined the rearrangement of the long-lived 1,1,2,3,4,5,6-heptamethylbenzenonium (I) [5-7] and 1-phenyl-1,2,3,4,5,6-hexamethylbenzenonium (II) ions [6, 8], when applied as their salts (anion $AlCl_4^-$) on alumina surfaces. That the structures of the ions (I) and (II) remained unchanged on the surfaces was shown by the observation that the PMR spectra of solutions obtained by extracting the salts from the alumina correspond to those reported in the literature [5, 6, 8]. In the case of ion (I), it was possible to obtain the ^{13}C NMR spectrum of the salt applied to alumina (Fig. 1). The similarities of the chemical shifts in the ^{13}C NMR spectra of this ion on alumina and in solution [6] indicates that the structure of the ion does not undergo any appreciable change when applied to the carrier. To judge from the signal width at half height in the NMR spectrum of (I), which is relatively small (270-510 Hz) for solids, the (I) ion on alumina is highly mobile, and the small differences between these values for carbons of the same type probably indicate that the latter are situated at approximately the same distance from the carrier surface (cf. [9].

It would be expected that the ion (I) on an alumina surface, as in solution [6, 7], would undergo degenerate rearragement by a 1,2-shift of the methyl group (1):



(Ia,b)

R = CH_3 (a), CHD_2 (b).

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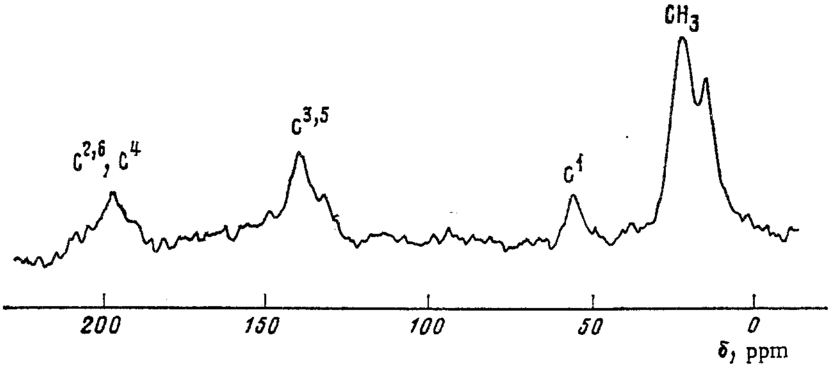

Fig. 1. ^{13}C NMR spectrum (50.32 MHz) of the tetrachloroaluminate ion (I) applied to Al_2O_3.

TABLE 1. Kinetic Characteristics of the 1,2-Shift of the Methyl Group in 1-R-1,2,3,4,5,6-Hexamethylbenzenonium Ions

R	Solvent, counterion	State	$k \cdot 10^4$, sec^{-1} (°C)[a]	E_a, kcal/mole	lg A	$k/k_{CH_2Cl_2}$	
						−20°	−70°
Me	$AlCl_4^-$	On Al_2O_3	17,8±1,5 (−23), 5,18±0,51 (−32,1), 2,02±0,25 (−40), 0,121±0,005 (−58), 0,0168±0,0004 (−70)	15,0±0,2	10,3±0,2	1,2	3,0
	$AlCl_4^-$ [b]	Crystal	0,544 (−20), 0,00320 (−70)	10,5±0,2	4,8±0,2	0,03	0,57
	CH_2Cl_2, $AlCl_4^-$ [b]	Solution	18,0 (−20), 0,00563 (−70)	16,5±0,1	11,5±0,1	1,00	1,00
	HSO_3Cl, SO_3Cl^- [c]	»	15,4 (−20), 0,00210 (−70)	18,2±0,6	12,9±0,4	0,86	0,37
	CF_3COOH, CF_3COO^- [c]	»	16,5 (−20), 0,00203 (−70)	18,4±0,8	13,1±0,6	0,92	0,36
Ph	$AlCl_4^-$	On Al_2O_3	7,99±0,45 (−13)			3,5[d]	
	CH_2Cl_2, $AlCl_4^-$	Solution	2,31±0,24 (−13)			1,0[d]	

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[a] The rate constants were found by averaging 2-3 measurements when R = Me, and 3-6 when R = Ph. In the remaining cases, k was calculated using the Arrhenius equation.
[b] Data from [7].
[c] Data from [6].
[d] At −13°C.

In fact, in the ^1H and ^2H NMR spectra of solutions obtained by extracting the tetrachloroaluminate ion (Ib) from the alumina surface with dichloromethane at −80°C after maintaining the salt on the carrier at −23 to −70°C, redistribution of the intensities of the methyl group signals was seen, similar to that found on examining the rearrangement in solution [7]. The kinetics of this redistribution correspond to scheme (1), assuming that the 1-methyl groups are equivalent, and the probability of their transfer to atoms C^2 and C^6 is equal, and also that isotope effects may be neglected [7, 8]. The rate constants for the 1,2-shift of the methyl group (Table 1) were calculated from the equation

$$\frac{S_p}{S_o} = \frac{a + bz^c + dz^i + lz^j}{2a + mz^c + nz^i + pz^j}$$

where S_p and S_o are the integral intensities of the signals for the 4- and 2,6-CHD_2 group in the ^2H NMR spectra, respectively; $z = e^{-2kt}$; k is the rate constant for the 1,2 shift; t is time; $a = 0.143$, $b = 0.255$, $c = 0.753$, $d = 0.209$, $i = 2.444$, $\ell = 0.189$, $j = 3.802$, $m = -0.113$, $n = -0.378$, $p = 0.236$. Treatment of these data by least squares using the Arrhenius equation (Fig. 2) gave the kinetic parameters shown in Table 1.

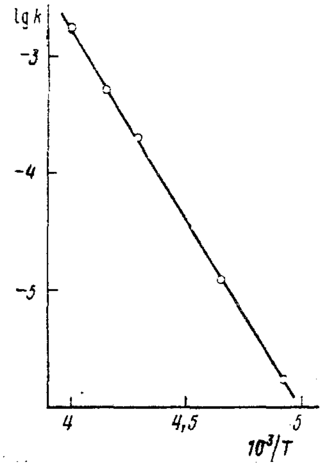
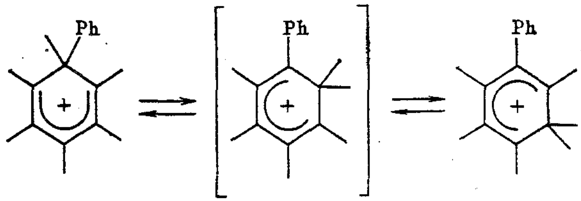


Fig. 2. Plot of log k for the rate of the 1,2-shift of the methyl groups in tetrachloroaluminate ion (I), applied to alumina, versus T^{-1}.

Attention is drawn to the fact that the values found for the Arrhenius parameters are intermediate between those for solutions and for the crystalline state. The decrease in the value of E_a as compared with that in solution may be due to interaction between the partial positive charge on the migrating group with the negative charges on the anions and with the basic centers of alumina, while the decrease in the value of log A is probably due to restrictions of the degrees of freedom of the atoms of the cation on reaching the transition state [7]. The resultant effect of the alumina surface on the rearrangement of the ion (I) is such that, unlike the crystalline state, on the carrier surface there is some acceleration of the 1,2-shift as compared with the solution (Table 1).

As mentioned above, the possibility of the existence of carbocations as intermediates in reactions on acidic heterogeneous catalysts is of fundamental importance for the theory and practice of heterogeneous catalysis [1-4]. As confirmation of the formation of carbocations in reactions of this type, it has recently been suggested that a criterion is the similarity of the energies of activation of the isomerization on a heterogeneous catalyst and in solution in superacids [3], in which the formation of carbocations has been reliably established. Our finding that there is a considerable decrease in the activation energy of the 1,2-shift in cation (I) on passing from the solution in HSO_3Cl to heterogeneous conditions (ΔE_a = 3.2 kcal/mole) shows that this criterion should be used with great caution.

The influence of the carrier surface on the nondegenerate carbocation rearrangement has been examined using the ion (II). In solution, this ion undergoes both degenerate and nondegenerate rearrangement, resulting in all likelihood from successive 1,2-shifts of the methyl group (2) [8]:



(II) (III)

In contrast, the tetrachloroaluminate ion (II) in the crystalline state does not undergo nondegenerate rearrangement [10]. For this reason, the possibility of the occurrence of nondegenerate rearrangement in the long-lived carbocation on the surface of a heterogeneous catalyst is of special interest.

When the ion (II), applied as the tetrachloroaluminate to alumina, is kept for a certain length of time at −13°C, the PMR spectra of the solutions obtained by extraction of the salt show, in addition to signals for the ion (II), signals for the rearranged ion (III). The rate constants for the rearrangement of the ion (II) to (III), both on alumina and in solution, follow a kinetic equation for a reversible first-order reaction, the rate of rearrangement on the carrier being greater than in solution (Table 1). Since the conversion of ion (II) into (III) on alumina is less exoenergetic than in solution [$K_{Al_2O_3}$ (−13°C) = 3.0, $K_{CH_2Cl_2}$ (−13°C) = 4.8], the observed acceleration is clearly due to a reduction in the internal barrier to rearrangement [11]. The results for the increase in the rate of the degenerate rearrangement of the ion (I) on passing from solution to a surface is in agreement with this assumption.

We have thus obtained for the first time experimental evidence of the catalytic effect of the surface of a solid carrier on the rearrangement of long-lived carbocations.

EXPERIMENTAL

The ^2H and ^{13}C NMR spectra of the ion (I) and the ^1H spectra of cations (II) and (III) were obtained on Bruker WP-200-SY, Bruker HX-90, and Varian A-56/10A spectrometers.

The alumina used was Brockman II neutral alumina from Reanal, 160-200 mesh, calcined in vacuo (1 mm, 500°C, 6 h). SO_2 was prepared as in [12], dichloromethane purified as in [10], and pure grade $AlCl_3$ was twice sublimed.

1-Dideuteromethylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (IV) was obtained from 1,2,4,5,6,6-hexamethyl-3-keto-1,4-cyclohexadiene (V) [13] as in [14], described for 1-methylene-4-phenyl-2,3,4,5,6-pentamethyl-2,5-cyclohexadiene. The molar ratio CD_3I:Mg:(V) was 5:5:1, the deuterium content of the CD_3I being 99.5 at. %. The PMR spectrum of (IV) was similar to that of the nondeuterated analog [5, 6], except that the signal for the methyl group was virtually absent.

(I) Tetrachloroaluminate on Alumina. Aluminum chloride (0.194 g) was dissolved at −20°C in 5 ml of SO_2, cooled to −196°C, and 0.259 g of the triene (IV) added. The mixture was warmed with stirring to −80°C, and dry HCl passed through. The resulting solution was frozen by cooling to −196°C, and 4.43 g of alumina added under argon. The mixture was warmed to −80°C and allowed to stand at this temperature for 2 h. Subsequently the SO_2 was removed by filtration followed by evacuation (10^{-4}-10^{-5} mm) at −70 to −65°C for 15.5 h. The amount of (I) tetrachloroaluminate on the alumina was 7.4% by weight, and the residual SO_2 was less than 0.6%.

The samples of (I) tetrachloroaluminate used to record the ^{13}C NMR spectra were those used in the kinetic measurements.

(II) Tetrachloroaluminate on Alumina. To 2.86 g of alumina was added under argon 0.082 g of crystalline (II) tetrachloroaluminate, prepared as described in [10], cooled to −80°C, and 3 ml of SO_2 added. When solution was complete, the mixture was kept for 2 h at −80°C, and the SO_2 removed by filtration, followed by evacuation (10^{-4}-10^{-5} mm) for 11 h. The amount of (II) tetrachloroaluminate on the alumina was 2.7%.

Kinetic Measurements of the Rearrangement of Ions (I) and (II) on Alumina. The ion salts prepared above (0.1-0.3 g) were placed in NMR ampuls at −80°C under chilled helium. The ampuls were kept at the required temperature (to within ±0.3°C), cooled to −80°C, extracted with dichloromethane or SO_2 [for cations (I) and (II), respectively], and the NMR spectra of the solutions recorded.

Kinetic Measurements of the Rearrangement of Ion (II) to (III) in Solution. A solution of (II) tetrachloroaluminate in dichloromethane (C 4%) was prepared at −50°C, kept in a cryostat at −13°C (to within ±0.3°C), and the PMR spectrum recorded at −50°C.

CONCLUSIONS

1. Acceleration of the degenerate and nondegenerate rearrangement of long-lived 1-R-1,2,3,4,5,6-hexamethylbenzenium ions (R = Me, Ph) on alumina surfaces as compared with solutions has been observed.

2. These results contradict the criterion of the involvement of carbocations as intermediates in heterogeneous catalytic processes, which requires that the activation energies of the acid-catalyzed isomerization of hydrocarbons under homogeneous and heterogeneous conditions should be similar.

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EXPLOSIVE CHEMICAL TRANSFORMATIONS OF 4-BROMO-2,4,6-TRI-TERT-BUTYLCYCLOHEXA-2,5-DIENE-1-ONE IN STRONG UNIAXIAL COMPRESSION

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Explosive chemical transformations in strong uniaxial compression are methodologically most convenient for studying the specific reactivity in the solid phase. The extremely high rates [1, 2], the possibility of altering the structural direction, as well as the acute shortage of experimental data necessary for the physicochemical interpretation of explosive events, have stimulated increasing interest in explosive transformations.

The present study is part of a cycle of studies of organochemical transformations in conditions of high pressure and different types of strains and concerns explosive transformations of 4-bromo-2,4,6-tri-tert-butylcyclohexa-2,5-dien-1-one (I) in strong uniaxial compression.

EXPERIMENTAL

Substance (I) was synthesized by the standard method from 2,4,6-tri-tert-butylphenol (II) and bromine in the two-phase ether + H_2O system with intense stirring and was purified by two low-temperature crystallizations from hexane; λ_{max} 245 nm corresponds to a p-quinoline structure. Chromatographically pure samples of 2-bromo-4,6-di-tert-butylphenol (III) [3], phenol (II), 2,6-di-tert-butylphenol (IV), and 4-bromo-2,6-di-tert-butylphenol (V) [4] were used as standards.

The experiments were conducted on an apparatus of the Bridgman anvil type [5]. Pellets 15 mm in diameter and 1.5-3 mm thick molded from (I) ground into powder were compressed up to the pressure at which an explosion occurred, accompanied by a strong noise and dispersion of the substance. To study the explosive transformation of binary systems of (I) + (IV) and (I) + PPh_3 separately, the substances ground into powder were used in equimolar ratios and pellets 15 mm in diameter and 3 mm thick were molded from the prepared mixture and then compressed up to the explosion pressure. The exploded samples were analyzed by TLC on Silufol UV-254 in hexane or pentane. Separation of the starting (I) and the products of its explosive transformation, identified as (II) and (III), was conducted by the same method.

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