Reports of the Academy of Sciences of the USSR

CHEMISTRY

1965

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 165, No. 5

UDC 66.062.22

CHEMISTRY

Yu. G. Bundel, V. A. Savin, A. A. Lubovich, Academician O. A. Reutov

ON THE EFFECT OF THE WATER CONTENT OF THE MEDIUM ON THE TYPE OF HYDRIDE SHIFTS AND THE DEGREE OF ISOMERIZATION IN THE ACETOLYSIS OF DEUTEROCYCLOHEXYL *p*-TOLUENESULFONATES

In the course of a systematic study of the isomerization of cyclohexyl cations by hydride shifts, we found different degrees of this isomerization during the acetolysis and formolysis of cyclohexyl-2,6-H_2^2-*p*-toluenesulfonates in anhydrous media (1). These differences are explained by the different lifetimes of the carbocation formed in media of differing nucleophilicity and ionizing ability. Cope (2) similarly explained the increase, observed in the formolysis of cyclooctyl brosylate, in the percentage of 1,5-shift of the hydride ion (up to 60%, compared with 55% in the case of acetolysis).

Fig. 1

Fig. 2

We also noted that, on going to formolysis, along with an increase in the total percentage of isomerization, there is a change in the ratio of the 1,2- and 1,3-types of hydride shifts: in acetolysis the corresponding values are 44 and 20%, and in formolysis, 60 and 11.7%. These data indicate that a change in the ionizing ability of the solvent does not favor the occurrence of hydride shifts of different types to the same extent.

In the present work we investigated the dependence of the type and degree of hydride shifts in the cyclohexyl system on the ionizing ability of the medium, using for the solvolysis of cyclohexyl-2,6-H_2^2-*p*-toluenesulfonate acetic acid with different water contents (in the presence of a molar amount of potassium acetate). The position of the label in the solvolysis products and the type and degree of isomerization were determined according to the scheme described earlier (^{1}). The results of the study are presented graphically in Fig. 1.

Analysis of the data presented in the graph shows that, analogously to what occurs on going from acetolysis to formolysis, the effect of water content on the degree of isomerization of the 1,2- and 1,3-types is different. The 1,2-shift decreases monotonically with increasing water content, whereas the 1,3-shift has a maximum value, equal to 33%, in the region of acid concentrations of 97–98%.

To confirm the presence of a maximum value of the 1—3 shift of the hydride ion in a system with a different position of the label, we studied the isomerization during acetolysis of cyclohexyl-1-H_1^2 *p*-toluenesulfonate in media of different water content (Fig. 2).

It is evident from the graph in Fig. 2 that, for a different absolute magnitude of the hydride-ion shift, which is a consequence of the secondary isotope effect of deuterium in position 1* (^{1,3}), the change in the degree of isomerization of the 1,3 type with increasing water content of the medium has the same form as in the case of the α-deuterated system, with a maximum in the region of acid concentrations of about 98%.

Uinstein showed in a series of works (^{4}) that, owing to its low ionizing power, anhydrous acetic acid is a medium that favors the formation of ion pairs to the greatest extent, whereas the formation of free (solvated) carbonium ions is relatively unlikely. An increase in the ionizing power of the medium upon addition of water to anhydrous acetic acid should lead to a shift of the equilibria of scheme (1) to the right and to an increase in the content of the solvated ion in this system.

$$\mathrm{R{-}OTs} \rightleftarrows \mathrm{R^{\oplus}OTs^{\ominus}} \rightleftarrows \mathrm{R^{\oplus}\|OTs^{\ominus}} \to \mathrm{R^{+} + OTs^{-}} \qquad (1)$$

A number of authors have shown (^{5,6}) that in phenonium ions 1,2-migration is often carried out in the state of an ion pair, accompanied by return of the anion of the leaving group. In all probability, such a scheme of isomerization also occurs in the case of 1,2-shifts of the hydride ion. As for the 1,3-shift, for it, as follows from the data of the present work, there must exist some optimum degree of ionization associated with the participation of a certain number of water molecules in the solvation of the ion. The difference between 1,2- and 1,3-shifts in this respect may be connected with the fact that shifts from positions 2 and 3 are favored by different conformational and stereoelectronic factors, among which the main role should be played by the optimum (and different for each of the types of shifts) conditions for orientation of the axis of the free *p*-orbital relative to the breaking C—H bond. This orientation is different in a planar (free) carbonium ion and in an ion that is part of an ion pair and has a nonplanar structure.

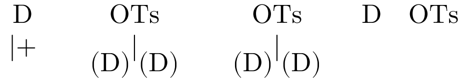
The decrease in the degree of 1,3-migration upon going from the optimum concentration (97—98%) to media of higher water content is explained by a decrease in the lifetime of the ion as a result of the increased probability of attack by the charged nucleophile CH_3COO^- at a higher degree of charge separation. The absence of sharp changes in the degree of isomerization (of both types) in the concentration range 86—94% indicates that

In this interval there are no longer appreciable changes in the degree of solvation or in the lifetime of the ion. In this region the water content in the acid is evidently sufficient for complete ionization and for the formation of a solvate shell consisting only of water molecules. In a system of this kind, the ratio of the amounts of alcohol and acetate formed during solvolysis is determined by competition between water (less nucleophilic, but located in the immediate vicinity of the ion) and the acetate ion (more nucleophilic, but forced to "break through" the solvate shell consisting of water molecules) (7). We investigated the composition of the products of aqueous acetolysis of cyclohexyl *p*-toluenesulfonate by gas-liquid chromatography and found that, at acetic acid concentrations of 86 and 91%, the ratio of the amounts of cyclohexanol and cyclohexyl acetate remains constant, approximately equal to 1 : 4, whereas at a concentration of 96.6% (corresponding to the maximum value of the 1,3-hydride-ion shift) this ratio has a clearly pronounced maximum (Fig. 3).

Fig. 3

---

* It is natural to expect differences in the ratio of types of hydride shifts (and also in the total degree of isomerization) in work with cyclohexanol tosylates labeled with deuterium in different positions. Obviously, in the case of the α-deuterated compound (II) the conditions are favorable for a 1,2-hydride shift, because cation I, formed as a result of the 1,2-shift, is thermodynamically more stable than the other possible ones (owing to the positive inductive effect of deuterium). It may be assumed that in the case of tosylate III, deuterated in position 3, the conditions are more favorable for a 1,3-hydride shift, since precisely as a result of this shift the stable cation I is formed. In work with tosylate IV, labeled with deuterium in position 1, the overall percentage of isomerization should be lowest, since the stable cation I is formed directly upon ionization of the tosylate.



$$\overset{\text{D}}{|+} \qquad \overset{\text{OTs}}{(\text{D})|(\text{D})} \qquad \overset{\text{OTs}}{(\text{D})|(\text{D})} \qquad \text{D} \quad \text{OTs}$$

(I) (II) (III) (IV)

Fig. 3

Figure 3: Fig. 3

Apparently this coincidence is not accidental; it indicates that, at a water content of 2–3 wt.%, the degree of ionization of the tosylate is such that the probability of nucleophilic attack by water molecules from the solvate shell is greatest. When the water content is decreased (in the range 0–2%), the percentage of alcohol formation decreases because water molecules take an ever smaller part in the formation of the solvate shell. The concomitant decrease in the degree of ionization of the ion pair causes a decrease in the extent of the 1,3-hydride-ion shift.

Moscow State University
named after M. V. Lomonosov

Received
28 V 1965

REFERENCES

1. Yu. G. Bundel' , V. A. Savin, A. A. Lyubovich, *Vestn. Moskovsk. univ., khim.*, No. 3, ser. 2, 85 (1965).
2. A. C. Cope, D. M. Gale, *J. Am. Chem. Soc.*, **85**, 3747 (1963).
3. E. A. Halevi, *Tetrahedron*, **1**, 174 (1957).
4. S. Winstein, E. Clippinger et al., *J. Am. Chem. Soc.*, **76**, 2597 (1954).
5. S. Winstein, G. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958); S. Winstein, K. Kliuedinst, *J. Am. Chem. Soc.*, **83**, 885 (1961).
6. D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2129 (1952).
7. D. Denney, B. Goldstein, *J. Am. Chem. Soc.*, **79**, 4948 (1957).
8. A. Streitwieser, *Solvolytic Displacement Reactions*, N. Y., 1962.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.