M. S. KISTENEVA, Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN

1962

SovietRxiv

Abstract

Full Text

Chemistry

M. S. KISTENEVA, Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN

KINETICS OF THE ALKYLATION OF 2-ACETYLMETHYLENE-3-ETHYLBENZTHIAZOLINE

On the question of seven-membered activated complexes

In work (¹), the interaction of acetylmethylene derivatives of N-substituted heterocyclic bases with alkylating agents, for example with alkyl halides and dimethyl sulfate, was studied. It was shown that quaternary salts of β-alkoxyalkenyl derivatives of heterocyclic bases are thereby obtained, according to the reaction:

$$\text{(I)} \quad \text{2-acetylmethylene-3-ethylbenzthiazoline} \; + \; \mathrm{CH_3J}$$

$$= \; \text{(II)} \quad \text{quaternary } \beta\text{-methoxyalkenyl salt} \; + \; \mathrm{J^-}$$

Thus alkylation proceeds not at the ring nitrogen atom, but at the carbonyl oxygen. The reason, possibly, is that in the initial compound (I), owing to conjugation, nitrogen bears a certain positive charge and is already partially tetravalent, corresponding to an sp^3 state, as may be represented by formula (III)

(III) zwitterionic conjugated form of 2-acetylmethylene-3-ethylbenzthiazoline, with N^+ in the ring and O^- in the acetyl group.

This type of conjugation is well known for urea, where the hybridization and spatial configuration are determined by the polar structure (all atoms, including the hydrogen atoms, lie in one plane), for acid amides, for the peptide bond, and for enamines (²), where it is demonstrated by chemical behavior and by an increased dipole moment. As a result, under the action of methyl iodide or dimethyl sulfate the methyl group attaches to the carbonyl oxygen, and not to nitrogen. The structure of the activated complex in such O-alkylation is somewhat different from that in the reaction of amines with alkyl halides. In the latter case, if the reaction is second order, the $\mathrm{CH_3J}$ molecule approaches the amine with its carbon atom, screened by three hydrogen atoms. During the reaction the hydrogen atoms move to the other side of the carbon (turning inside out like an umbrella in a strong wind), while the halide is split off as an ion. In our case the mechanism is somewhat different. If this is a molecular reaction proceeding upon collision of two molecules, then in the activated complex the alkyl halide approaches the carbonyl oxygen, and redistribution of bonds along the chain takes place

$$-\mathrm{N}-\mathrm{C}=\mathrm{CH}-\mathrm{C}_{\mathrm{O}}$$

In the reaction through a seven-membered activated complex, alternation of bonds being broken and bonds being formed occurs; the electron is displaced toward iodine, ···

which passes into the state of a negative ion and the I—C bond is broken. It was of interest to investigate the kinetics of this reaction and to determine whether it indeed proceeds by second order, and also to determine the enthalpy ΔH^* and entropy ΔS^* of the activated complex for the case of O-alkylation.

We studied the kinetics of the reaction between I and methyl iodide in methyl alcohol, and also between the same substance and dimethyl sulfate in benzene.

In the case of the reaction with methyl iodide, a 0.1 molar solution of I in methanol was heated with CH_3J (excess of 10–100%). Samples were taken at intervals of 3–5 hours, and the iodine ion was titrated with silver nitrate. The measurements were carried out at 45, 55, and 60°.

In the reaction with dimethyl sulfate, the latter was heated with a benzene solution of I. The concentration of I was 0.33 mole/l, and that of dimethyl sulfate 0.48 mole/l. The experiments lasted 1.5; 2; 3; 4; 5; 6; 7 hours. After the heating was completed, the solution was diluted with ether, the precipitate II was filtered off and dried to constant weight. The experiments were carried out at 40, 45, 55, and 60° and showed that in both cases the reaction proceeds by second order. For the reaction with methyl iodide, the following values of the specific rates were obtained (time is expressed in seconds, and concentration in gram-moles per 1 l): at 45° $K = 2.79 \cdot 10^{-6}$, at 55° $K = 6.17 \cdot 10^{-6}$, and at 60° $K = 9.73 \cdot 10^{-6}$.

From these data, for the Arrhenius equation one obtains

$$K = 10^6 e^{-16800/RT}.$$

Application of the theory of the activated complex gives for the enthalpy ΔH^*_{298} 16200 cal. and for the entropy ΔS^*_{298} −32.6 e.u.

For the reaction with dimethyl sulfate, the following values of the specific rates were obtained: at 40° $K = 1.24 \cdot 10^{-5}$, at 45° $K = 2.03 \cdot 10^{-5}$, at 55° $K = 4.5 \cdot 10^{-5}$, and at 60° $K = 6.36 \cdot 10^{-5}$. From these data we obtain $K = 2.2 \cdot 10^7 e^{-17500/RT}$. Accordingly $\Delta H^*_{298} = 16900$ cal. and $\Delta S^*_{298} = -26.5$ e.u. Let us note that in the reactions of amines with alkyl halides, i.e. in N-alkylation, the activation energy most often lies in the range 12000–10000 cal. (3). As is seen from our data, in the case of O-alkylation the activation energy is increased approximately to 17000 cal. This is apparently connected with the fact that, upon addition to nitrogen in the amine molecule, no bonds are broken, and electron transfer to the halide is facilitated by the donor properties of the amine nitrogen, which in the reaction passes into a new hybrid state sp^3 with stronger bonds. If the nitrogen in the initial state is partially positively charged, as in (III), no addition to nitrogen occurs, and the alkyl adds to oxygen with an increased activation energy. It must be thought that here the circumstance plays a role that in O-alkylation the π-bond of the carbonyl group is broken, for without this the addition of the alkyl is impossible. As for the C—halogen bond, it is broken in any type of alkylation, but electron transfer is more easily effected in the presence of amine nitrogen. Small pre-exponential factors (negative entropies of the activated complex) are characteristic of all reactions of formation of quaternary ammonium salts. In the N-alkylation reactions considered in another work (3), ΔS^* lies in the range from -32 to -46, and ΔF^* from 20000 to 24000 cal. In our case of O-alkylation, $\Delta S^* = -32.6$ and -26.5, and ΔF^* 26000–25000 cal.

Thus, the greatest difference between the two types of alkylation is observed in the activation energies and, correspondingly, in ΔH^*.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
29 V 1962

REFERENCES

1. N. N. Sveshnikov, I. I. Levkoev et al., DAN, 88, 281 (1953).
2. A. N. Shidlovskii, Ya. K. Syrkin, N. K. Kochetkov, Izv. AN SSSR, OKhN, 1956, 254.
3. Ya. K. Syrkin, M. A. Gubareva, Acta Physico-Chimica, 8, 236 (1938).

Note: Figure translations are in progress. See original paper for figures.

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