KINETICS OF *tert*-BUTYLAMINOLYSIS OF *n*-BUTYL TRICHLOROACETATE IN HEPTANE

Agu-Tõnis TALVIK, Imbi TALVIK, and Ants TUULMETS

Institute of Organic Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia; tuulmets@chem.ut.ee

Abstract. Kinetics of *tert*-butylaminolysis of *n*-butyl trichloroacetate was investigated in heptane solutions by taking samples and analysing them for both ester and *n*-butyl alcohol content by gas–liquid chromatography. A bulky *tert*-butyl group in the amine causes a great decrease in the reaction rate and the aminolysis becomes reversible. The equilibrium constant is dependent on the composition of the reaction medium. The reaction is second-order in amine and the apparent activation energy is close to zero. These findings are compatible with the reaction mechanism adopted for less bulky amines. Thus, a shift of the rate-determining step of the reaction in case of *tert*-butylamine can be excluded.

Key words: aminolysis of esters, reaction mechanism, solvent effects.

INTRODUCTION

The mechanism of ester aminolysis in aprotic media was analysed by Menger and Smith [1]. For ester aminolysis the following general scheme was proposed: ester + amine $\rightleftharpoons$ intermediate $\rightarrow$ products. The collapse of the tetrahedral intermediate was adopted as the rate-determining step of the reaction.

The breakdown of the intermediate may be uncatalyzed or it may be general base catalyzed by a second molecule of the amine or also by other bases. However, conclusions upon the mechanism of the aminolysis reaction have so far been drawn mainly from investigations of experimentally convenient esters with good leaving groups. For this reason a kinetic study of the aminolysis of aliphatic esters, never conducted before, was recently undertaken in this laboratory [2, 3]. Convincing evidence was gained in favour of cyclic transition states for both the first- and second-order (in amine) reactions in aprotic media.

The importance of the steric requirements of the reagents was also pointed at in our previous papers [2, 3]. The reaction appeared to be most susceptible to the steric encumbrance at the amine site [3]. These results were well in line with the assumption of cyclic transition states for the reaction. However, Druzian et. al [4] dealing with the aminolysis of trichloroarylethanones raised the question whether the steric bulk in amine might cause the initial amine attack on the carbonyl to become slower than the decomposition of the tetrahedral intermediate, thus shifting the rate-determining step of the aminolysis. For this reason we briefly resumed our kinetic study of the *tert*-butylaminolysis of *n*-butyl trichloroacetate [3]. In this paper we report the results of the kinetic investigation together with some additional observations on the features of the reaction.

EXPERIMENTAL

All the procedures were the same as described in our previous papers [2, 3]. The reaction was carried out in a stainless steel cell with two pits at its bottom. Into one of the hollows we placed a heptane solution of the ester and into the other, a solution containing the amine and the internal standard pentadecane in heptane, usually 1 cm^3 of both solutions. The reaction cell was thermostated, and the reaction was started with a vigorous shaking of the reactor. The initial concentration of the amine in the reaction mixture was from 0.56 up to 4.75 mol dm^{-3} and that of the ester was 0.027 mol dm^{-3}. Samples were taken with a microsyringe through the silicon-rubber membrane in the lid of the cell and immediately analysed with a gas–liquid chromatograph Tsvet (column 2.5 m × 3 mm). The concentration of the ester and that of the product alcohol were calculated and plotted against time. The initial rate of the reaction was determined as the slope of the tangent of the kinetic curve at the initial point of time.

RESULTS AND DISCUSSION

The kinetic measurements were carried out at different amine concentrations in the reaction mixture. Because of an extremely low reaction rate, lower amine concentrations could not be used. For the same reason and because a negative activation energy was expected, reaction temperatures 3 and 20°C were chosen. However, it appeared that the activation energy of the reaction was close to zero.

Second-order rate coefficients calculated from the initial rates of the reaction are presented in Table 1. The constants in the table are mean values obtained from 3 to 5 runs and both from the disappearance of the ester and from the formation of *n*-butanol.

Table 1. Second-order rate coefficients for *tert*-butylaminolysis of *n*-butyl trichloroacetate in heptane calculated from the initial rates of the reaction

Concentration of the amine, M	$k \times 10^5 \, dm^3 \, mol^{-1}s^{-1}$	
	3 °C (±1 °C)	20 °C (±0.1 °C)
0.56	0.43±0.12	0.47±0.03
0.83	–	1.2±0.2
1.12	–	1.2±0.2
2.36	–	0.76±0.04
4.75	0.69±0.13	0.75±0.04

– Not determined.

In some cases the course of the reaction was followed practically up to the end. Differently from the reactions investigated previously [2, 3] the *tert*-butylaminolysis at the amine concentration equal to 0.56 M appeared to be less shifted to far right and an equilibrium constant $K = 0.038$ at 20±1 °C could be estimated. At 3 °C a slight precipitation occurring during the reaction did not allow a reliable determination of the equilibrium. At a higher amine content in the reaction medium, equal to 4.75 M, a first-order irreversible reaction was observed. Thus, the equilibrium constant of the reaction varies with changes in the medium composition. Obviously the observed shift in the position of the equilibrium should be assigned to an increase in the equilibrium constant value with an increase in medium polarity caused by large additions of the amine.

A similar medium effect can be observed for the reactivity data in Table 1. At lower amine concentrations, a higher reaction order, at least the second order in amine, can be recognized. Further additions of the amine suppress the reaction rate evidently due to an increase in the polarity of the medium. Indeed, we found earlier [2] a rate decrease by the polarity and π-basicity of the solvents and also an accelerating effect of the polarizability of solvents for ester aminolyses. Replacement of heptane by *tert*-butyl amine does not alter the polarizability of the medium but considerably enhances the polarity of the binary mixture, thus reducing the rate of the reaction.

The data in Table 1 indicate a great decrease in the rate of aminolysis in case of *tert*-butyl amine (about 4000 times in comparison with *n*-butyl amine, cf. ref. 3). However, the reaction order and the observed activation energy (close to zero or slightly positive) are compatible with the mechanism adopted for reactions of esters with less bulky amines [3]. Thus, the shift of the rate-determining step of the aminolysis of esters as the amine becomes more sterically hindered can be excluded at least for amines as bulky as *tert*-butyl amine.

ACKNOWLEDGEMENT

REFERENCES

1. Menger, F. M. & Smith, J. H. Mechanism of ester aminolyses in aprotic solvents. *J. Am. Chem. Soc.*, 1972, **94**, 3824–3829.
2. Talvik, A.-T., Tuulmets, A. & Vaino, E. Kinetics and mechanism of aminolysis of aliphatic esters in aprotic solvents. *J. Phys. Org. Chem.*, 1999, **12**, 747–750.
3. Tuulmets, A. & Talvik, A.-T. Activation energies of aminolysis of aliphatic esters in aprotic media. *ACH Models in Chem.*, 2000, **137**, in press.
4. Druzian, J., Zuero, C., Rezende, M. C. & Nome, F. Aminolysis of 2,2,2-trichloro-1-arylethanones in aprotic solvents. *J. Org. Chem.*, 1989, **54**, 4767–4771.

TRIKLOROETAANHAPPE *n*-BUTÜÜLESTRI JA *tert*-BUTÜÜLAMIINI REAKTSIOONI KINEETIKA HEPTAANI KESKKONNAS

Agu-Tõnis TALVIK, Imbi TALVIK ja Ants TUULMETS

Trikloroetaanhappe *n*-butüülestri ja *tert*-butüülamiini reaktsiooni kineetikat heptaani keskkonnas on uuritud proovide võtmise meetodil, määrates estri ja *n*-butüülalkoholi sisaldust proovides gaasi-vedelikukromatograafia abil. Suur *tert*-butüülrühm amiini molekulis põhjustab reaktsioonikiiruse olulise kahanemise ning aminolüüs muutub pöörduvaks. Tasakaalukonstant sõltub reaktsioonikeskkonna koostisest. Reaktsioon on amiini järgi teist järku ning näilik aktiveerimisenergia on nullilähedane. Need tähelepanekud on kooskõlas mehhanismiga, mida peetakse kehtivaks vähemmahukate amiinide reaktsioonide korral. Järelikult on kiirust limiteeriva staadiumi nihe *tert*-butüülamiini korral välistatud.