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## GAS CHROMATOGRAPHIC STUDY OF THE REACTIVITY OF TOLUIDINES TOWARDS AN ACTIVE DIESTER

M. PANK, A. KOGERMAN, O. KIRRET and G. RAJALO

*Institute of Chemistry of the Academy of Sciences of the Estonian S.S.R., 15 Akadeemia Tee, 200026 Tallinn 26 (U.S.S.R.)*

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### SUMMARY

The rate of reaction of *o*-, *m*- and *p*-toluidine with diphenyl sebacate was determined under plug-flow gas chromatographic conditions. Owing to the large excess of diphenyl sebacate, which acted simultaneously as the liquid phase, the reaction is of pseudo-first order. Velocity constants, Arrhenius parameters and activation energies were calculated.

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### INTRODUCTION

Gas chromatography (GC) has been a particularly useful method for the study of the kinetics and reactivities of chemical compounds, using two basic techniques. The simpler and more widely technique involves the periodic collection of samples of a reaction mixture and their subsequent analysis in a gas chromatograph, while the plug-flow GC method involves carrying out both the chemical reaction and the analysis in the GC system. Plug-flow GC is most often used in the study of heterogeneous catalytic reactions.

Few papers have been published on the study of the kinetics of liquid-phase reactions by this method. The first time this direct method was used for the study of the kinetics of liquid-phase reactions was in 1961 by Gil-Av and Herzberg-Minzly in investigations of the reaction of dienes with chloromaleic anhydride<sup>1</sup>. Berezkin and co-workers studied the esterification of alcohols<sup>2</sup> and the reactions of maleic anhydride with dienes<sup>3,4</sup>.

In this work, an attempt has been made to use plug-flow GC for the characterization of irreversible polycondensation reactions. In recent years, considerable interest has arisen in the mechanisms and physico-chemical aspects of polycondensation reactions, owing to increased applications of irreversible polycondensation reactions in which the so-called active esters of carboxylic acids are used as source materials. Active esters are widely used for the synthesis of peptides by the methods of Wieland *et al.*<sup>5</sup> and Schwyzer *et al.*<sup>6</sup>, and include phenyl, thiophenyl and nitrophenyl esters of carboxylic acids.

In this paper are given results on the kinetics of irreversible polycondensation

reactions based on model compounds, obtained by plug-flow GC. Diphenyl sebacate was used as the "active" monomer in these reactions.

## EXPERIMENTAL

An experimental chromatograph (Special Construction Bureau of the Estonian Academy of Sciences) equipped with a flame ionization detector was used, with a stainless-steel column (2 m × 4 mm I.D.). Chromaton N, AW-DMCS (0.20–0.25 mm) (Lachema, Brno, Czechoslovakia) was used as the solid carrier, on which 7% diphenyl sebacate (10 cm) and 7% Apiezon L (190 cm) were coated. The volatile reactant *o*-, *m*- or *p*-toluidine together with the standard (diisoamyl ether) entered the reactor column as a plug. Different degrees of conversion of the amines were obtained by varying the rate of flow. The contact time of the reactants was determined by the difference between the retention time of the amine and the dead time of the reactor column. The dependence of the reaction rate on contact time was measured at 92° and the temperature dependence of the reaction rate was determined over the range 82.5–115°.

## RESULTS

Chromatograms of the toluidines are shown in Fig. 1. As a result of the chromatographic conditions used, with a large excess of diphenyl sebacate, its reaction with the toluidines is of pseudo-first order (Fig. 2) and can be represented by the equation  $k_1 t_{cor} = \ln(C_0/C)$ , where  $t_{cor}$  is the contact time of the amine in the diphenyl sebacate liquid phase.

As the volume of the volatile reactant in GC is proportional to the peak area, it is convenient to determine the concentration change by the internal standard method. In this instance, equation  $k_1 t_{cor} = 2.3 \log (S/S_{st})_0 / (S/S_{st})_x$  applies, where

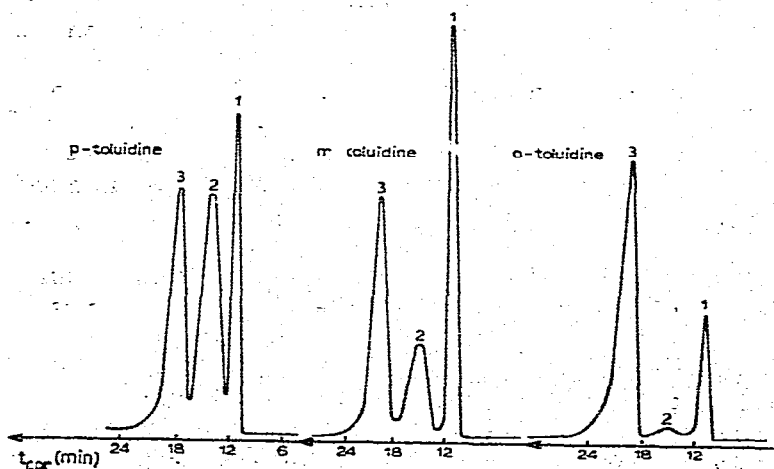


Fig. 1. Chromatograms of *o*-, *m*- and *p*-toluidine after passing through the reactor column at 92°. 1 = Diisoamyl ether; 2 = phenol (reaction product); 3 = amine.

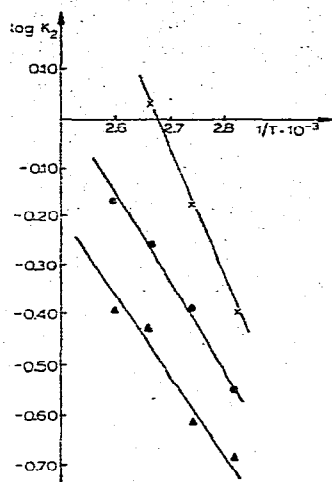
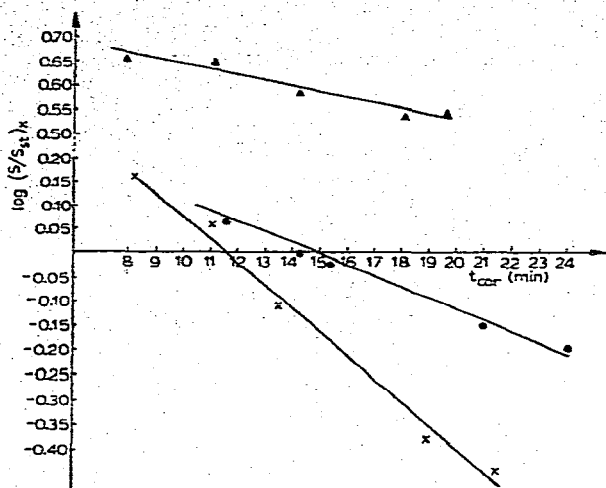


Fig. 2. Plot of  $\log (S/S_{st})_x$  against contact time at  $92^\circ$ .  $\Delta$ , *o*-Toluidine;  $\bullet$ , *m*-toluidine,  $\times$ , *p*-toluidine.

Fig. 3. Dependence of  $\log k_2$  on  $1/T$ . Symbols as in Fig. 2.

$(S/S_{st})_x$  is the ratio of the peak area of the reacting compound to that of the standard and  $(S/S_{st})_0$  is the ratio of the same areas before the reaction.

The ester concentration in the chromatographic column remains practically constant as  $C_2$ . Therefore, for the bimolecular reaction studied, the velocity constant is  $k_2 = k_1/2 C_2$ . The velocity constants were calculated with a computer and the constants  $k_1$  and  $k_2$  and the correlation constants ( $K$ ) are given in Table I.

TABLE I  
EXPERIMENTAL VALUES OF KINETIC PARAMETERS

Amine	Rate constants		$K$	$\log A$	$E$ (kcal/mole)
	$k_1 \cdot 10^{-2}$ ( $\text{min}^{-1}$ )	$k_2$ ( $1/\text{mole} \cdot \text{min}$ )			
<i>o</i> -Toluidine	2.59	0.244	0.9748	4.6	8.0
<i>m</i> -Toluidine	5.29	0.409	0.9852	5.2	8.9
<i>p</i> -Toluidine	11.03	0.674	0.9852	7.2	11.9

As shown in Table I and Fig. 2, the toluidines with the methyl groups in different positions differ in reactivity. The highest velocity constants were shown by *p*-toluidine, while *o*-toluidine reacted much slowly under identical conditions owing the steric hindrance. *m*-Toluidine had an intermediate reactivity.

The temperature dependences of the velocity constants were used for calculating the activation energy of the reactions investigated. The dependence of  $\log k_2$  on  $1/T$  for the amidation reactions of diphenyl sebacate is illustrated in Fig. 3. The activation energies ( $E$ ) were calculated from the slopes of the curves, while the intercept on the ordinate at  $1/T = 0$  gave the Arrhenius parameters ( $A$ ) (Table I).

The plug-flow GC method for kinetic studies is comparatively rapid and requires only very small amounts of substances, and also impurities are removed as the reactant moves along the column.

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