



## NEW INFORMATION ON THE SOLVOLYSIS OF TERTIARY BUTYL HALIDES

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The solvolysis of *tert*-butyl halides, *t*-BuX, releases ions,  $H^+$  and  $X^-$ , leading to an increase in conductance,  $G$ . Accurate kinetic data may be obtained by measuring the dependence of  $G$  on time.

According to the Swinbourne method for first order reactions, the linear plot  $G_t = a + b G_{t+\Delta t}$ , where  $\Delta t$  is a constant period of time, leads to the rate constant  $k$  ( $k = \ln b / \Delta t$ ) [1]. The application of this method to the solvolytic reactions of *t*-BuX in alcohols, using the same  $\Delta t$ , the same number of pairs of points equally spaced and different regions of the reaction, support the conclusion that  $k$  values remain approximately constant during a period of time which corresponds to 90-95% of the maximum value of  $G$ . In Figure 1, (a) and (b), and in Table 1 this behaviour is exemplified for two particular systems (two

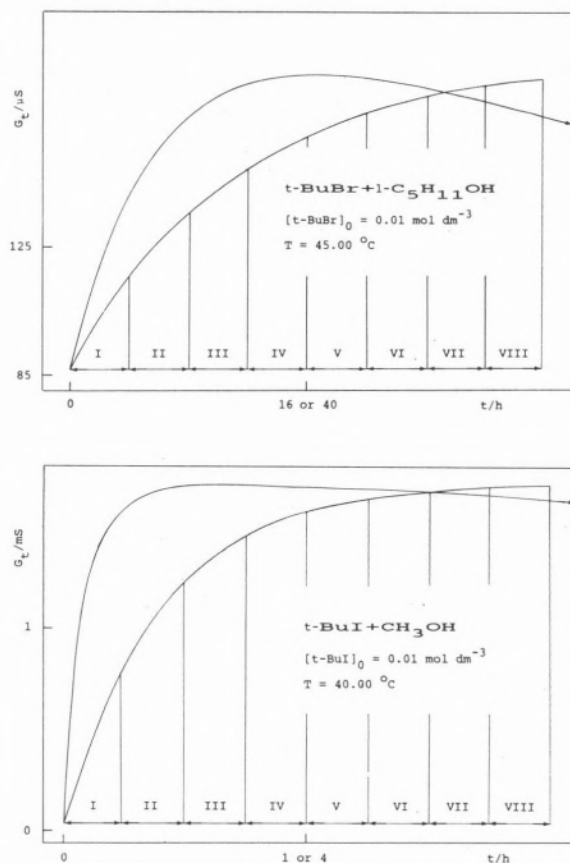


Figure 1

Solvolytic reactions of *t*-BuX in alcohols

Table 1  
Solvolytic reactions of *t*-BuX in alcohols  
Dependence of *k* on reaction time

SYSTEMS	G <sub>t</sub>	G <sub>t+Δt</sub>	10 <sup>5</sup> k/s <sup>-1</sup>	10 <sup>5</sup> σk/s <sup>-1</sup>
<i>t</i> -BuBr + 1-C <sub>5</sub> H <sub>11</sub> OH	I	II	2.31	0.02
	II	III	2.23	0.01
	III	IV	2.23	0.03
	IV	V	2.41	0.06
	V	VI	2.71	0.05
	VI	VII	2.75	0.21
	VII	VIII	3.24	0.38
<i>t</i> -BuI + CH <sub>3</sub> OH	I	II	71.7	0.3
	II	III	70.7	0.1
	III	IV	71.0	0.1
	IV	V	71.6	0.4
	V	VI	74.0	1.5
	VI	VII	75.6	3.9
	VII	VIII	86.1	5.8

scales of time were used). This is in accordance with the accurate work of Biordi and Moelwyn-Hughes [2]. The rate constant of the *t*-BuI methanolysis at 40°C, interpolated from reported data, is  $7.18 \times 10^{-4} \text{ s}^{-1}$  [2].

However, if reactions are followed beyond about 90-95% reaction, *G* no longer behaves in a typical «first-order manner», but reaches a maximum value and then starts to decrease.

On the other hand, induction periods have been observed for the hydrolysis of *t*-BuCl followed at low concentrations [3,4]. Although several independent explanations have already been advanced, acid catalytic effect [3], low solubility of the substrate in water [5], buffering effect of water molecular structure [6] and of dissolved carbon dioxide [4], the hypothesis of the existence of an intermediate, as foreseen by Albery and Robinson [7], should not be excluded.

It is important to realise that the form of the rate equation which applies in the early states of the solvolytic reactions of *tert*-butyl halides is not the same as that for equilibrium conditions.

If first order is assumed, as it is usually done, rate constant values should be obtained under conditions such that neither early states of the reaction nor the states approaching the equilibrium are included in the calculations.

$\Delta^*C_p$  values reported for this type of systems are quite large and have a marked temperature dependence, suggesting a complex mechanism [8,9]. The present results support this assumption.

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