

CÉSAR A NUNES VIANA

LÍDIA M. P. C. ALBUQUERQUE

M. ISABEL DA S. PEREIRA

Faculdade de Ciências de Lisboa  
Centro de Estudos de Radioquímica  
C. E. E. N. — I. A. C.  
Lisboa



## KINETICS OF CATALYSED SOLVOLYSIS

### II—Concentration effect on the kinetics of the methanolysis of *tert*-butyl chloride

*The concentration influence on the kinetics of tert-butyl chloride methanolysis is studied. It is shown that the rate constant increases with concentration in the range 0.001–0.05 M. The results present an approximately linear variation when*

*$\log \vec{k}$  is plotted against  $\left( \frac{\sqrt{c}}{1-\sqrt{c}} - 0.2 c \right)$  and the experimental gradient is near the theoretical one.*

## 1 — INTRODUCTION

The catalytic effect of hydrochloric acid on the kinetics of the hydrolysis of *tert*-butyl chloride was studied by us in an earlier work (1) Ionic strength and homo-ionic effects associated to that catalysis are distinguished, and it is recognized that solution ionic strength exerts the main influence on the reaction rate. The results are discussed on the basis of Debye-Hückel theory, and they show that both the hydrochloric acid initially introduced and the one formed during the reaction have large influence on the kinetics of the catalysis. Therefore, in such reaction, there is an important auto-catalytic effect on account of the hydrochloric acid which is formed during the reaction. In this paper the concentration effect on the rate constant of the methanolysis of *tert*-butyl chloride is studied, and the values of the rate constants are related with solution ionic strengths.

## 2 — EXPERIMENTAL

The technique used here was essentially the *in situ* conductimetric, described before (1). The analysis of conductance data to obtain rate constants was based on GUGGENHEIM'S method (2), and the required conductance-concentration linear dependence was observed through all the concentration range (0.001–0.05 M). Its demonstration may be based on either HARTLEY'S, WYNNE-JONES' and SCHEDLOVSKY'S equations (3-5) applied to hydrochloric acid methanolic solutions by a similar argument to the one used for water solutions (1). The same general procedure for solution preparation and *tert*-butyl chloride purification was followed here. B. D. H. methanol «ARISTAR» (maximum water content, 1.000 p.p.m.) was used without further purification. At each concentration four experiments were, at least, carried out, and the experimental temperature was always  $25 \pm 0.01^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Reaction rate constant as a function of initial concentration of *tert*-butyl chloride is presented in the second column of Table I, and in fig. 1.

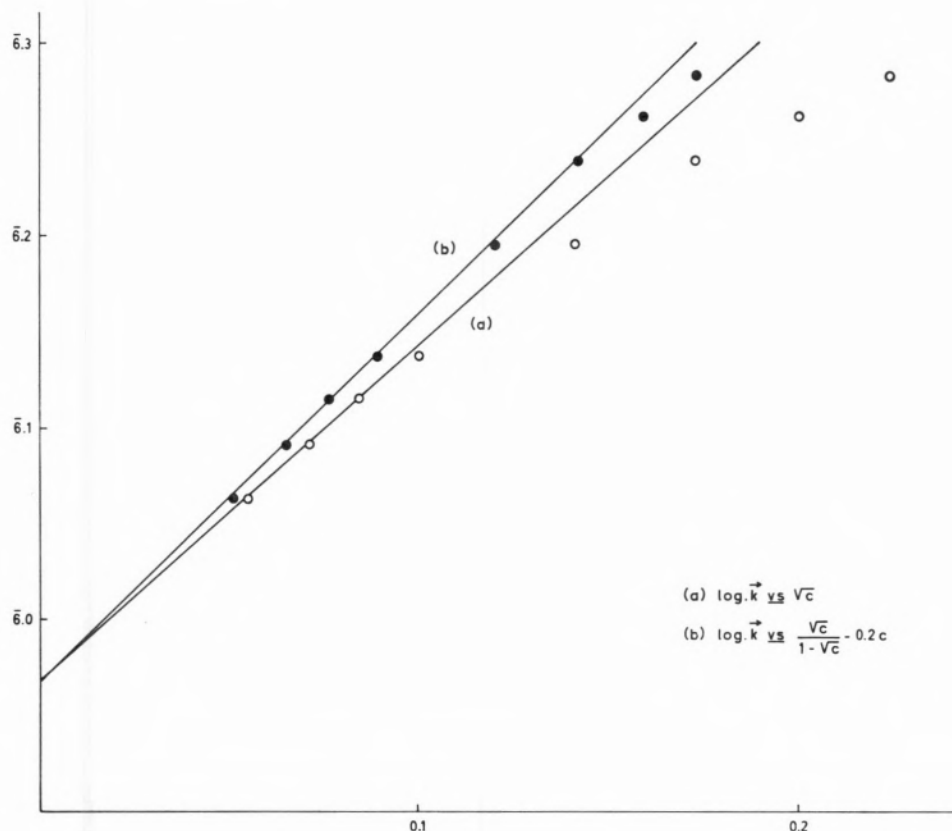


Fig. 1

These results are accurate within a standard deviation, generally less than 1 %, and they are in good agreement within each set of experiments at same concentration, the mean deviation being less than 1 %. Also our  $\vec{k}$  values are comparable to those obtained by other authors in analogous conditions (6,7).

It is clear that, for the concentration range used, the rate constant always increases with concentration. This means that ionic strength effect predominates over the homo-ionic effect on account of the amount of hydrochloric acid being formed during the reaction. Therefore, the variation of  $\vec{k}$  with concentration may be interpreted by Debye-Hückel theory, taking into account convenient adaptations for the concentration of the electrolytic system. The equation,

$$\ln \vec{k} = \ln k_o + 2A z_i z_j \frac{\sqrt{I}}{1 - \sqrt{I}} - 0.2I \quad (1)$$

adapted from DAVIES' equation (8) has been shown to be useful for aqueous solutions at moderate concentrations (1). In fig. 1b the correspondent

$\log \vec{k} - \left( \frac{\sqrt{c}}{1 - \sqrt{c}} - 0.2c \right)$  variation is plotted for

the present system and it is seen that this plot is almost linear for the whole concentration range; only for the highest concentrations there are large deviations, but, in these conditions, the homo-ionic effect must be quite important. The experimental gradient is 2.76 which compares well with the theoretical value which is  $2A = 3.2$  (1). In fig. 1a, on what  $\log \vec{k} - \sqrt{c}$  dependence is plotted, the deviations from linearity are larger for higher concentrations, being the experimental gradient smaller than 2.76; its value is 2.50.

(1) A was calculated from the expression

$$A = \frac{(2\pi)^{3/2} N^2 e^3}{2.3026 (\Sigma kT)^{3/2} \cdot (1000)^{1/2}}$$

From the present results, as well as from those presented in the former work of this series (1), it seems that the Debye-Hückel theory, expanded to moderately concentrated solutions, can be useful on the interpretation of concentration effects on reaction rate of solvolytic reactions of alkyl chlorides. However, when concentration increases to larger values than those we used here, the rate can decrease as a consequence of a gradually more important homo-ionic effect.

Extrapolation to zero concentration leads, by application of a least square method (the same method was used to obtain the experimental gradients), to about the same value of  $\log \bar{k} = 7.6290$  when  $\log \bar{k}$  is plotted *versus*  $\sqrt{c}$ , and 7.6305 when  $\log \bar{k} - \left( \frac{\sqrt{c}}{1-\sqrt{c}} - 0.2c \right)$  variation is considered. It leads to a mean rate constant of  $4.261 \cdot 10^{-7} \text{ sec}^{-1}$ , which must be the value of  $\bar{k}$  «free» of catalytic effects other than those produced by the solvent.

Table I

Concentration (mol. l <sup>-1</sup> )	$\bar{k}$ (s <sup>-1</sup> ) . 10 <sup>6</sup>	$\log \bar{k}$	$\sqrt{c}$	$\frac{\sqrt{c}}{1-\sqrt{c}} - 0.2c$
0.001	1.055	6.02325	0.033	0.031
0.003	1.156	6.06296	0.055	0.051
0.005	1.234	6.09132	0.071	0.065
0.007	1.303	6.11494	0.084	0.076
0.010	1.372	6.13735	0.100	0.089
0.020	1.668	6.19535	0.141	0.120
0.030	1.732	6.23855	0.173	0.142
0.040	1.826	6.26150	0.200	0.159
0.050	1.916	6.28240	0.224	0.173

## LIST OF SIMBOLS

- $\rightarrow$   
 $k$  — rate constant  
 $\rightarrow$   
 $k_0$  — rate constant at infinite dilution  
 $A$  — Debye-Hückel coefficient  
 $z_i, z_j$  — charge numbers  
 $I$  — solution ionic strength  
 $c$  — concentration (mole. l<sup>-1</sup>)  
 $N$  — Avogadro's number  
 $e$  — electronic charge  
 $k$  — Boltzman's constant  
 $\epsilon$  — solvent dielectric constant  
 $T$  — absolute temperature

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## RESUMO

Estuda-se o efeito da concentração sobre a cinética da metanólise do cloreto de butilo terciário. Observa-se que a constante de velocidade aumenta com a concentração no intervalo 0,001 — 0,05 M. Os resultados mostram uma variação aproximadamente linear quando se faz a representação

gráfica  $\log \bar{k}$  versus  $\left( \frac{\sqrt{c}}{1-\sqrt{c}} - 0,2c \right)$ , sendo o valor do gradiente experimental próximo do teórico.