

Faculdade de Ciências  
Centro de Estudos de Radioquímica  
Comissão de Estudos de Energia Nuclear (I.A.C.)  
Lisboa 2



## KINETICS OF CATALYSED SOLVOLYSIS

### I—Factors which control salt and Hydrochloric acid Hydrolysis of *tertiary*-butyl chloride

*Ionic strength and homo-ionic effects are studied relatively to the kinetics of acid and salt hydrolysis of tert-butyl chloride. In the concentration range 0.002-0.04 M, the ionic strength effect is the most important as the rate constant always increases with concentration. Results from acid catalysis are analysed*

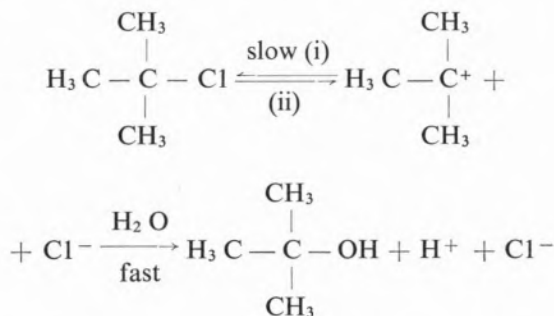
*on basis of  $\log \vec{k}$  variations with  $\sqrt{c}$ ,  $\left(\frac{\sqrt{c}}{1-\sqrt{c}} - 0.2 c\right)$*

*and pH, and it is seen they approximately follows what would theoretically be expected. Salt catalysis is essentially distinguished by the catalyst anionic radii.*

## 1—INTRODUCTION

This is the first of a series of works on catalysed solvolysis of alkyl chlorides. This paper is specially concerned with the influence of hydrochloric acid and several potassium salts on the kinetics of the *tertiary*-butyl chloride hydrolysis. In such systems, the solvent has its own catalytic effect which is generally interpreted as a function of its dielectric constant. When an ionic reactant is present in the solution, that effect must be reinforced and, certainly, it has a specific role.

According to INGOLD (1), the hydrolysis or *tertiary*-butyl chloride is an uni-molecular reaction. However, other authors (2-9) admit the existence of intermediate mechanisms ( $S_N12$ ) or the alternate participation of  $S_N1$  and  $S_N2$  mechanisms for reactions of this type. In our system, the predominance, or the tendency, must be the uni-molecular mechanism, considering the very high dielectric constant of water, as well as the great dipole moment of its molecules. When ionic reactants are added to the solution, at high dilutions, their degrees of dissociation or ionization are nearly one and a large amount of charges can be concentrated around the activated complex; consequently, the dipole moments of the reactant molecules increase, and the dissociation is therefore stimulated. Simultaneously, another phenomenon can occur: if the catalyst is a chloride there is homo-ionic effect and the reaction equilibrium is displaced to the opposite direction of dissociation. A better understanding of these effects can be obtained from the following reaction scheme:



If  $a$  is the initial concentration of *tertiary*-butyl

<sup>(1)</sup> Present address: Laboratório de Química — Faculdade de Ciências — Universidade de Luanda.

chloride and  $x$  the chloride ion concentration resulting from its dissociation, the reaction rate is given (10) by

$$\frac{dx}{dt} = \vec{k} \cdot (a - x) \cdot \left[ 1 + \alpha_1 (c + x) \right]^{-1} \quad (1)$$

where  $\vec{k}$  is the rate constant and  $[1 + \alpha_1 (c + x)]^{-1}$  is a factor which account for the catalytic effect.  $\alpha_1$  is a constant which measures the competitive power of the chloride ion and the water to react with the carbonium ion;  $c$  is the initial concentration of hydrochloric acid. If we consider that this acid is not completely dissociated and ionized, the degree of ionization,  $\alpha_2$ , must be introduced and expression (1) becomes,

$$\frac{dx}{dt} = \vec{k} \cdot (a - x) \cdot \left[ 1 + \alpha_1 (\alpha_2 c + x) \right]^{-1} \quad (2)$$

As we have already pointed out, besides mass law effects, electrostatic effects related to ionic strength must also be observed. According to BATEMANN, HUGHES and INGOLD (11), the ionic atmospheres stabilise the transition state. The reaction should be therefore accelerated since the activated complex attracts the ionic atmospheres and its dipole moment is increased.

The situations which essentially can be put are indicated in Table I:

Table I

Reactant mixture	Homo-ionic effect	Ionic strength effect
Without initial concentration of acid or salt	Progressive decreasing of specific rate	Progressive increasing of specific rate
With initial concentration of homo-ionic acid or salt	Retardation	Acceleration
With initial concentration of non-homo-ionic acid or salt	No initial effect	Acceleration

Those catalytic effects are also dependent on the radii and charges of the ions or molecules which are the catalytic agents. The interactions between charges and dipoles generated in solution are generally interpreted by KIRKWOOD's theory (12) which, in a simplified form, can be expressed by the equation

$$\ln \vec{k} = \ln \frac{kT}{h} - \frac{e^2}{2\epsilon RT} \left[ \sum_i \frac{z_i^2}{r_i} - \frac{z_*^2}{r_*} \right] - \frac{3}{4\epsilon RT} \left[ \sum_i \frac{\mu_i^2}{r_i^3} - \frac{\mu_*^2}{r_*^3} \right] \quad (3)$$

where  $k$  represents the Boltzman's constant;  $h$ , the Planck's constant;  $T$ , the absolute temperature;  $R$ , the gas constant;  $\epsilon$ , the solvent dielectric constant;  $z_i$ ,  $z_*$  the charge numbers,  $\mu_i$ ,  $\mu_*$  the dipole moments, and  $r_i$ ,  $r_*$  the molecular radii of the reactants and the activated complex, respectively. Other equations based on Kirkwood's theory have been proposed, namely by LAIDLER and EYRING (13), by AMIS (14) and by VIANA and REIS (15).

As a summary, the ionic strength effect together with the increasing of the dipole moments will lead to an increase of the reaction rate constant. On the other hand, equations 1 and 2 show that the reaction rate must gradually decrease with increasing HCl concentration.

In this paper, concerning aqueous solutions of *tertiary*-butyl chloride at constant concentration, we intent to investigate the relative importance of both effects when different amounts of hydrochloric acid and several potassium salts, at constant concentrations, are added.

## 2 — EXPERIMENTAL

The kinetic experiments were based on observation of the variation of HCl concentration with time. The conductimetric method was chosen and an auto-balanced bridge Wayne-Kerr B-641 was used. The precision of this instrument for conductimetric determinations is better than 0.1 %, and its sensivity always permitted to obtain the experimental conductances with at least five figures, when working in connexion with a digital voltmeter (Hewlett Packard 3480 A).

GUGGENHEIM's method (16) was used for determining the first order rate constants, whose validity is dependent on the hypothesis that solution conductances are linearly proportional to hydrochloric acid concentrations. This is the case for the present situation. In fact, let us consider the Schedlovsky's equation (17) for HCl aqueous solutions, at 25°C and one atmosphere,

$$\frac{\Lambda + 59.78\sqrt{c}}{1 - 0.2273\sqrt{c}} = 426.16 + 169c \quad (4)$$

where  $\Lambda$  represents the HCl equivalent conductance for concentration  $c$ . This equation can easily take another form

$$\lambda_x M = c - 0.297c^{3/2} + 0.397c^2 - 0.090c^{5/2} \quad (5)$$

where  $\lambda_x$  is the solution conductance, and  $M$  is a constant dependent on the cell-solution system.

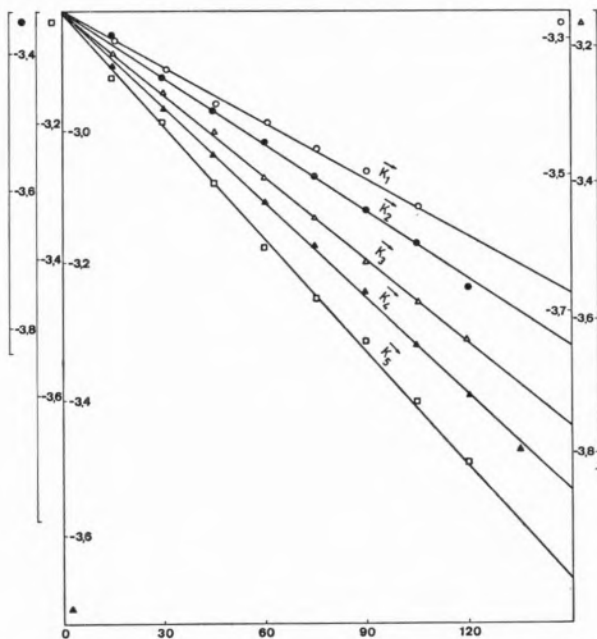


Fig. 1 — Influence of HCl on the kinetics of tert-butyl chloride hydrolysis

$$\log \left( \frac{1}{Rt_i + \tau} - \frac{1}{Rt_i} \right) \text{ vs. time (sec.)}$$

- non-catalysed hydrolysis
- tert-butyl chloride in HCl 0.002 M
- △ tert-butyl chloride in HCl 0.005 M
- ▲ tert-butyl chloride in HCl 0.01 M
- tert-butyl chloride in HCl 0.02 M

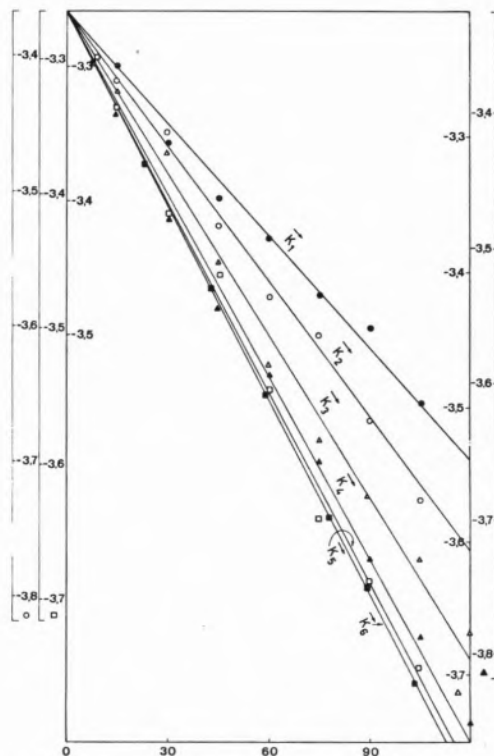


Fig. 2 — Influence of several salts on the kinetics of tert-butyl chloride hydrolysis

$$\log \left( \frac{1}{Rt_i + \tau} - \frac{1}{Rt_i} \right) \text{ vs. time (sec.)}$$

- non-catalysed hydrolysis
- tert-butyl chloride hydrolysis catalysed with KCl
- tert-butyl chloride hydrolysis catalysed with KBr
- △ tert-butyl chloride hydrolysis catalysed with KI
- ▲ tert-butyl chloride hydrolysis catalysed with  $K_3[Fe(CN)_6]$
- tert-butyl chloride hydrolysis catalysed with  $K_4[Fe(CN)_6]$

Solutions were always 0.02M in *tert*-butyl chloride at the beginning of each experiment and the HCl initial concentration was varied up to 0.02 M. For this concentration range, when  $c = 0.02$  M, the sum of three last terms of (5) is  $-6.10 \cdot 10^{-4}$  M, which is approximately 3 % of 0.02 M. However, this is one of the most unfavourable situations on the linear dependence of  $\lambda_x$  with  $c$ , and even in this case the differences of conductance will correspond to smaller concentrations since Guggenheim's method is based on differences of magnitudes which are proportional to concentrations relative to prefixed time-intervals—in our case, these time-intervals were between three and five minutes). Therefore, we can write in every case,

$$|c| \gg \left| -0.297c^{3/2} + 0.397c^2 - 0.090c^{5/2} \right| \quad (6)$$

We must note that the validity of this approximation is clearly justified on figs. 1 and 2 where  $\log(\lambda_{t_i+\tau} - \lambda_{t_i})$  is plotted against  $t_i$  ( $t_i$  being any time and  $\tau$  a pre-fixed time-interval) relatively to each HCl concentration. In every case, the plots are perfectly linear.

Oil baths of high electric resistance and low viscosity (SONAP STO/10), vigorously stirred were used as thermostats for electrolytic cells. The temperature control was assured by a toluene-mercury thermostat associated to an electronic relay. This system permitted a precision of  $0.01^\circ\text{C}$ . All the experiments were carried out at  $30.00^\circ\text{C}$ . The electrolytic cell (fig. 3) has already been described by one of us (18); its electrodes were of bright platinum whose advantages have been pointed out elsewhere (18).

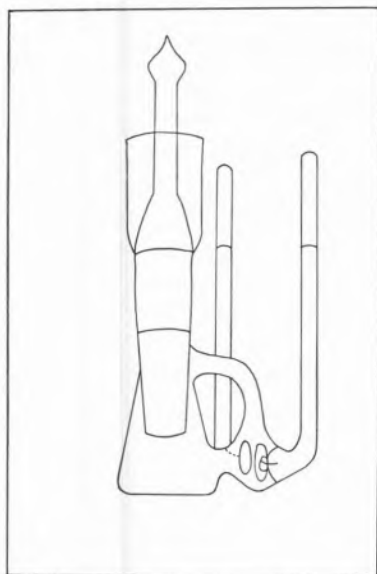


Fig. 3 — Conductance Cell.

Special care was dedicated to the purification of the reactants. Only very good and recently prepared conductivity water was used. The water was first boiled in a «Kottermann» apparatus and then two consecutive fractional distillations from potassium permanganate and barium hydroxide were performed. Proceeding this way, a specific conductivity of  $2.5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  was

reached. Hydrochloric acid solutions were prepared by distilling hydrogen chloride into water in an oxygen-free atmosphere, and standardized against borax (19). B. D. H. *tert*-butyl chloride was further purified by two consecutive fractional distillations (760 mm-Hg). For the first distillation, only the fraction distilling below  $50.5^\circ\text{C}$  was collected and for the second one, (carried out in presence of anhydrous sodium sulphate (4)), the fraction between  $50.3$  and  $50.4^\circ\text{C}$  was collected. The purified reactant was refractometrically tested and the refractive index was  $1.38570$  in agreement with tabulated values. Potassium salts used as catalysts, were B. D. H. Analar reagents (their degrees of purity were specified between  $99.5$  and  $99.8\%$ ), were twice recrystallized from conductivity water and then dried at  $180^\circ\text{C}$  for twelve hours, cooled and stored in a vacuum desiccator. The salt solutions, all made  $0.01 \text{ M}$ , were thermostated before addition of *tert*-butyl chloride.

All the glass material was washed with sulphochromic mixture and hot concentrated nitric acid, and, then, passed by hot conductivity water vapour for one to two hours; while hot, it was dried in a nitrogen stream. As the reactions were quite fast, the solvent (water + HCl or potassium salt) was thermostated to  $30.00^\circ\text{C}$  before adding the convenient amount of *tert*-butyl chloride to make the solution  $0.02 \text{ M}$ .

Four to six experiments were performed at each concentration.

### 3 — RESULTS AND DISCUSSION

The experimental values of the rate constants at each initial HCl concentration are presented in Table II.

Table II

$(\text{CHCl})_i \text{ (mole.l}^{-1}\text{)}$	$\vec{k} \text{ (s}^{-1}\text{)} \times 10^{-3}$
0.000	$2.675 \pm 0.044$
0.002	$3.140 \pm 0.050$
0.005	$3.955 \pm 0.047$
0.010	$4.745 \pm 0.037$
0.020	$5.465 \pm 0.032$



The rate constants correspondings to the introduction of several potassium salts in the solution are presented in Table III.

Table III

Salt	$\vec{k} \text{ (s}^{-1}) \times 10^{-3}$
Non-catalysed	
hydrolysis	$2.675 \pm 0.044$
KCl	$4.695 \pm 0.070$
KBr	$3.225 \pm 0.050$
KI	$4.015 \pm 0.050$
$K_4 \text{ Fe (CN)}_6$	$4.898 \pm 0.010$
$K_3 \text{ Fe (CN)}_6$	$4.753 \pm 0.073$

Before consideration is given to the significance of the results, their precision should be made plain. Although the reactions were all rather fast, the internal consistency of any one experiment was high; the corresponding standard deviation was generally 1 %. The results from each set of four to six independent measurements were also in good agreement, the mean deviation being less than 1.6 %. On the other hand, our  $\vec{k}$  value for neutral solvolysis is comparable to those obtained, in analogous conditions, by other authors (4,8). Comparison with other examples of catalysed hydrolysis is not possible owing to lack of data in the literature. However, the results obtained by us for *tert*-butyl chloride hydrolysis catalysed by potassium chloride (*tert*-butyl chloride, 0.02 M; KCl, 0.01 M) lead to a rate constant of  $4.73 \times 10^{-3} \text{ s}^{-1}$  which is very similar to  $\vec{k} = 4.745 \times 10^{-3} \text{ s}^{-1}$ , the rate constant when the initial concentration of hydrochloric acid was 0.01 M. It shows, most probably, that the catalytic effect is much less specific for cations than for anions at least when their external electronic structure is  $s^1$ . This point of view is corroborated by PANDA and NAYAK'S results (20) concerning *tert*-butyl chloride solvolysis in methanol-water mixtures when sodium and potassium chlorides and bromides are used as catalysts.

Fig. 1, as well as Table I, show that the rate constant clearly increases as the HCl concentration increases. Also, it increases when potassium salts

are in solution. Keeping our initial considerations in mind, this seems to indicate that the catalysis is mainly controlled by the ionic strength effect.

Therefore, the  $\vec{k}$  variation with catalysts concentration should be interpreted by the Debye-Hückell theory, taking into account the convenient adaptations for HCl concentrations. From the well-known Brönsted-Bjerrum equation,

$$\vec{k} = \vec{k}_o \frac{\gamma_i \cdot \gamma_j}{\gamma_*} \quad (7)$$

and using the DAVIES'S equation (21), which is applicable to dilute and moderately concentrated solutions, we can be led to:

$$\ln \vec{k} = \ln \vec{k}_o + 2A z_i z_j \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} + (\beta_i + \beta_j - \beta_* - 0.2) I \right\} \quad (8)$$

where  $z_i$  and  $z_j$  represent the charge numbers;  $\gamma_i$ ,  $\gamma_j$  and  $\gamma_*$ , the activities;  $I$ , the ionic strength; and  $\vec{k}_o$ , the rate constant for infinite dilution.  $A$ , is the Debye-Hückel coefficient;  $\beta_i$ ,  $\beta_j$  and  $\beta_*$ , whose sum is small in the case of ionic interactions, are constants inversely proportional to the ionic and the molecular radii;  $i$ ,  $j$  refer to ionic species and  $*$  refers to the activated complex. For dilute solutions, equation 8 can be simplified to

$$\ln \vec{k} = \ln \vec{k}_o + 2A z_i z_j \sqrt{I} \quad (9)$$

The application of this equation to the observed results shows (fig. 4a) a certain tendency towards linearity where  $\log \vec{k}$  is plotted against  $\sqrt{c}$ , though the deviations are quite large. However,  $c$ , in this plot, represents the initial concentration of HCl, i. e., the concentration before adding *tert*-butyl chloride. Nevertheless, when temperature equilibrium is reached, after the addition of *tert*-butyl chloride, some time is passed. It is, then, that measurements of solution conductances are started: by this time there is also some HCl resulting

from the hydrolysis of *tert*-butyl chloride and, clearly, this acid has some catalytic action.

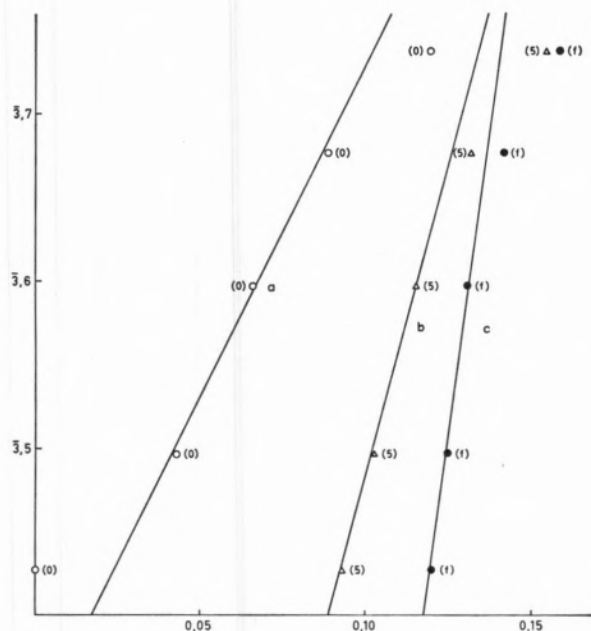


Fig. 4 — Hydrochloric acid hydrolysis of *tert*-butyl chloride

$\log k$  vs.  $\sqrt{c}$

a —  $\circ$   $c$ -initial concentration of HCl

b —  $\triangle$   $c$ -HCl concentration after 5 minutes of reaction

c —  $\bullet$   $c$ -HCl concentration assuming all *tert*-butyl chloride dissociated

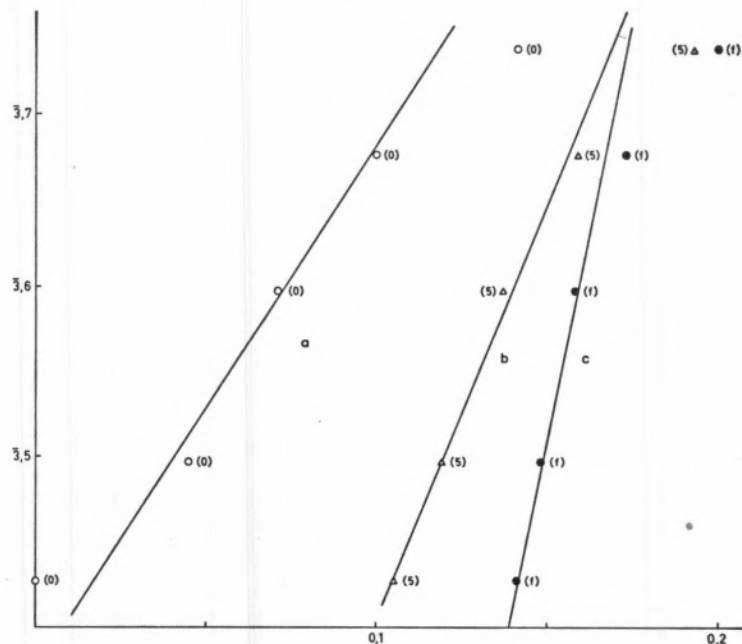


Fig. 5 — Hydrochloric acid hydrolysis of *tert*-butyl chloride

$\log k$  vs.  $\frac{\sqrt{c}}{1 + \sqrt{c}} - 0.2c$

a —  $\circ$   $c$ -initial concentration of HCl

b —  $\triangle$   $c$ -HCl concentration after 5 minutes of reaction

c —  $\bullet$   $c$ -HCl concentration assuming all *tert*-butyl chloride dissociated

Assuming that useful measurements of conductances can be made five minutes after adding the *tert*-butyl chloride, we can calculate the total amount of HCl, on a first order kinetics basis. These values are presented in the fourth column of Table IV, and they are quite different from those inscribed in the second column.

Table IV

$\log k$	$(\text{CHCl})_i$	$\sqrt{(\text{CHCl})_i}$	$(\text{CHCl})_5$	$\sqrt{(\text{CHCl})_5}$
3.4273	0.000	0.000	0.011 (036)	0.105 (1)
3.4969	0.002	0.045	0.014 (204)	0.119 (2)
3.5971	0.005	0.071	0.018 (894)	0.137 (4)
3.6763	0.010	0.100	0.025 (182)	0.158 (7)
3.7376	0.020	0.141	0.037 (118)	0.192 (7)

In fig. 4b we can see that the variation of  $\log k$  with  $\sqrt{(\text{CHCl})_5}$  is still linear, that the statistical deviations are much smaller, and that the slope is near the theoretical value which is unity. In fig. 4c it is represented a limit situation which corresponds to assume all *tert*-butyl chloride dissociated. A similar analysis is made in figs. 5a, 5b and 5c where, on DAVIES' equation (21) basis,

$\log \vec{k}$  is plotted versus  $\left(\frac{\sqrt{c}}{1 + \sqrt{c}} - 0.2c\right)$ . The conclusions are analogous, and the observed results, represented in fig. 5b, are even better aligned.

It can be therefore inferred that the catalytic effect is due not only to the HCl initially introduced but also to an important auto-catalytic effect which is a consequence of HCl being formed as the reaction proceeds. The point that corresponds to the higher hydrochloric acid concentration deviates considerably from linearity. This is, most probably, due to an appreciably large homo-ionic effect which, for larger concentrations, brings about a clear decrease of the specific rate of the reaction.

effects. However, as fig. 5b shows, that slope is, in absolute value, slightly smaller which is, most probably, due to the existence of same anion in the reactant and in the catalyst.

The results presented in Table III show rate constants referring to the following concentrations: *tert*-butyl chloride, 0.02 M; potassium salts, always 0.01 M. It is evident that, in all the cases, the dissociation of *tert*-butyl chloride is stimulated by the catalysts as the lower rate constant is the one relative to the uncatalysed hydrolysis. As the molar concentrations are always the same, and the catalyst cation is always potassium ion, the main catalytic difference must be due to anionic differences of structure. Assuming essentially the same transition state

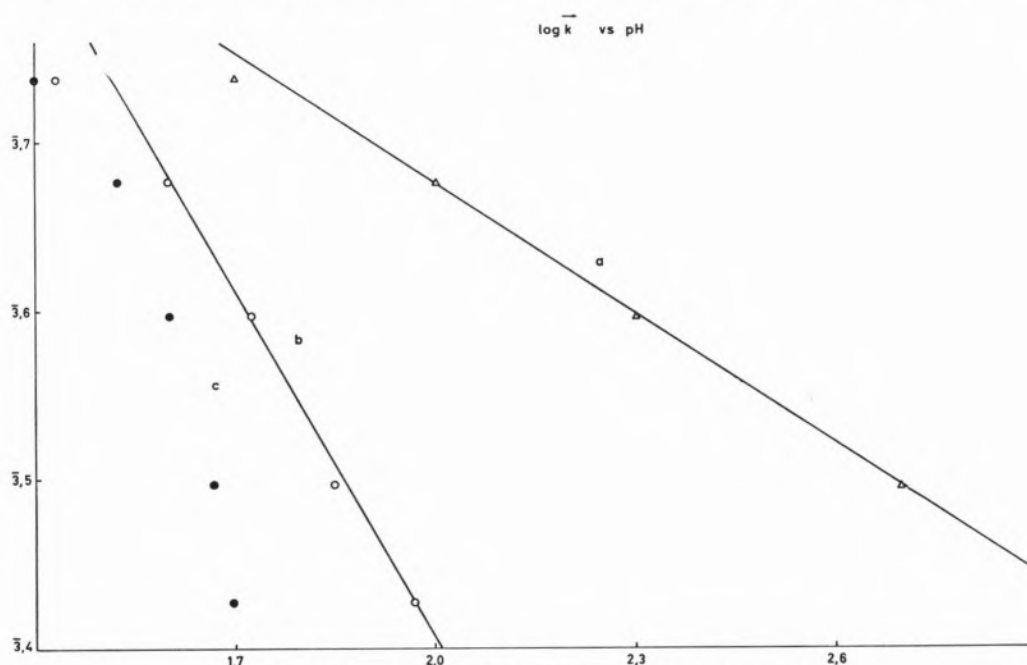


Fig. 6 — Hydrochloric acid hydrolysis of *tert*-butyl chloride: pH effect

$\log \vec{k}$  vs. pH

a —  $\triangle$  initial pH

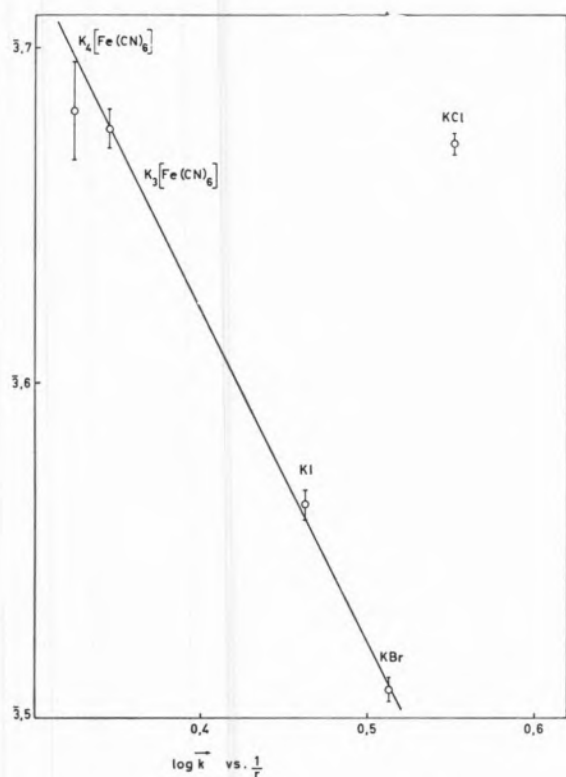
b —  $\circ$  pH after five minutes of reaction

c —  $\bullet$  pH assuming all *tert*-butyl chloride dissociates.

In figs. 6a, 6b and 6c, pH effect is studied and a, b and c indexes are, respectively, referred to the initial pH, the pH after five minutes of reaction and the final pH assuming all *tert*-butyl chloride dissociated.

According to BELL (22) the straight line slope should be equal to,  $-1$  since there are not homo-ionic

structure for all the cases, the anionic part of  $\sum_i \frac{z_i^2}{r_i}$  in the second term of equation 3 must be that one which, fundamentally, expresses rate constant differences. If this is so, the variation of  $\log \vec{k}$  versus  $\frac{Z}{r}$  (anion) is expected to be linear. However,

Fig. 7—Salt effect on *tert*-butyl chloride hydrolysis
$$\log k \text{ vs. } \frac{1}{r}$$

according to fig. 7, a linear variation is, most probably, found where  $\log k$  is plotted against  $\frac{1}{r}$  (anion). There is only one exception which is the point corresponding to the use of potassium chloride as a catalyst, and there the rate constant is much higher than should be expected. In fact, the rate constant ought to be much smaller, even below the alignment of points. That means that *tert*-butyl chloride dissociation is easier in this

case. This fact can be related to a larger number of chloride ions, than the other anions, being in competition with water molecules, to coordinate *tert*-butyl ions. It can, most probably, explain the linear variation of  $\log k$  with  $\frac{1}{r}$  instead of with  $\frac{z}{r}$ . This point of view is reinforced when reasons between *tert*-butyl ion radius and anion radius are considered. According to Table V, a tendency to octahedral symmetry seems to appear where crystals of several complexes of *tert*-butyl could be formed. In case of chloride ions the tendency appears to be for coordination index of eight. Assuming this as good, potassium salts with smaller anionic radii ( $F^-$ ,  $CN^-$ , etc.) also should have higher rate constants than those predicted in fig. 7. On the other hand, the variation of rate constant with temperature and pressure will lead to entropies and volumes of activation which, most probably, have important differences depending on the coordination index. Yet X-ray crystallography can clarify certain doubts on structural problems. All the corresponding works are, at the moment, in course in our laboratory.

The present results are considered by us simply as symptoms and no as irrefutable proofs. Nevertheless, the high dipole moment of *tert*-butyl chloride ( $\mu = 5.5$  Debye) and the small radius of *tert*-butyl ion suggests a tendency to polarization of negative charge which can lead to formation of coordinate bonds. A full theory concerned with these results is not yet possible. However, the following works using water and other solvents will, certainly, help to a better understanding of the present problems.

Table V

Ion	radius ( $\text{\AA}$ )	<i>tert</i> -butyl <sup>+</sup> radius/anionic radius
<i>tert</i> -butylon	1.39	—
chloride ion	1.81	0.552
bromide ion	1.95	0.513
iodid ion	2.16	0.463
ferrycyanide ion	2.90	0.345
ferrocyanide ion	3.06	0.324

## REFERENCES

- Ingold, C. K., «Structure and Mechanism in Organic Chemistry», Bell & Sons, Ltd, London, 1963, p. 317.
- Swain, C. G. and Scott, C., *J. Am. Chem. Soc.*, **75**, 141 (1953).
- Winstein, S. and Fainberg, A. H., *J. Am. Chem. Soc.*, **79**, 5937 (1957).
- Moelwyn-Hughes, E. A., *J. Chem. Soc.*, 1517 (1961).
- Hudson, R. F., *J. Chem. Soc.*, 4121 and 4130 (1955).



6. Robertson, R. E. and Hyne, R. F., *Can. J. Chem.*, **35**, 613 (1957).  
Robertson, R. E. and Hyne, R. F., *Can. J. Chem.*, **33**, 1544 (1955).  
Robertson, R. E. and Hyne, R. F., *Can. J. Chem.*, **34**, 863 (1956).
7. Ruber, D. J., Bingham, R. C., Harris, J. M., Fry, J. L. and Schleyer, P. R., *J. Am. Chem. Soc.*, **92**, 5977 (1970).
8. Moelwyn-Hughes, E. A., Robertson, R. E. and Sugamori, S., *J. Chem. Soc.*, 1965 (1965).
9. Hyne, J. B., Wills, R. and Wonkha, R. E., *J. Am. Chem. Soc.*, **84**, 2914 (1962).
10. Ingold, C. K., «Structure and Mechanism in Organic Chemistry», Bell & Sons, Ltd., London, 1963, p. 360.
11. Bateman, L. C., Church, M. G., Hughes, E. D., Ingold, C. K. and Taher, N. A., *J. Chem. Soc.*, 979 (1940).
12. Kirkwood, J. C., *J. Chem. Phys.*, **2**, 351 (1934).
13. Laidler, K. J. and Eyring, H., *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).
14. Amis, E. S., *J. Chem. Educ.*, **30**, 351 (1953).
15. Viana, C. A. N. and Reis, J. C. R., In preparation.
16. Guggenheim, E. A., *Phil. Mag.*, **2**, 538 (1926).
17. Schedlovsky, O., Browv, A. S. and McInnes, D. A., *Trans. Electrochem. Soc.*, 165 (1934).
18. Viana, C. A. N., «Ph. D. Thesis», Univ. Southampton, 1966, p. 76.
19. Vogel, A., «A Text-Book of Quantitative Inorganic Analysis», 3.<sup>a</sup> ed. Longmans, London, 1961, p. 238.
20. Panda, B. B. and Nayak, B., *J. Indian Chem. Soc.*, **41**, 774 (1964).
21. Davies, C. W., *J. Chem. Soc.*, 2093 (1938).
22. Bell, R. P., «Acid-Base Catalysis», Claredon Press, Oxford, 1941.

## RESUMO

Estudam-se os efeitos de força iónica e de homo-iónico relativos à cinética das hidrólises ácida e salina do cloreto de butilo terciário. Observa-se que, no intervalo de concentrações 0,002 — 0,04 M, o efeito da força iónica é, dos dois, o mais importante, uma vez que a constante de velocidade aumenta sempre com a concentração. Os resultados da catálise ácida são analisados com base nas variações de  $\log \vec{k}$  com  $\sqrt{c}$ ,  $\left( \frac{\sqrt{c}}{1 - \sqrt{c}} - 0,2 c \right)$  e pH, verificando-se que elas seguem, de forma aproximada, o comportamento que, teòricamente, seria de esperar. A catálise salina é, essencialmente, caracterizada pelo raio aniónico do catalisador.