

TABLE 3

Thermal expansivity and compressibility of water-ethanol mixtures, and volumes of activation for the solvolysis of *t*-butyl chloride in these mixtures at 0 °C

| % v/v ethanol in water | $10^6 \alpha$<br>deg <sup>-1</sup> * | $10^6 \kappa$<br>bar <sup>-1</sup> * | $\Delta V^\ddagger$<br>cm <sup>3</sup> mole <sup>-1</sup> | $T\alpha\Delta V^\ddagger/\kappa$<br>cal mole <sup>-1</sup> |
|------------------------|--------------------------------------|--------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|
| 0                      | -68.1                                | 50.3                                 | $-2.0 \pm 0.5$                                            | $18 \pm 5$                                                  |
| 10                     | 25.3                                 | 44.1                                 | $-7.0 \pm 1.0$                                            | $-26 \pm 5$                                                 |
| 25                     | 241                                  | 38.1                                 | $-13.2 \pm 0.6$                                           | $-545 \pm 50$                                               |
| 40                     | 625                                  | 44.3                                 | $-21.5 \pm 1.0$                                           | $-1979 \pm 100$                                             |

\*Values of  $\alpha$  and  $\kappa$  for water are from ref. 7, and for other solvents, from ref. 8.

TABLE 4

The activation parameters for the hydrolysis of *t*-butyl chloride in water-ethanol mixtures at 0 °C

| % v/v ethanol in water | $\Delta G_p^\ddagger$<br>cal mole <sup>-1</sup> | $\Delta H_p^\ddagger$<br>cal mole <sup>-1</sup><br>± 150 | $T\Delta S_p^\ddagger$<br>cal mole <sup>-1</sup><br>± 150 | $\Delta U_v^\ddagger$<br>cal mole <sup>-1</sup><br>± ~ 200 | $T\Delta S_v^\ddagger$<br>cal mole <sup>-1</sup><br>± ~ 200 |
|------------------------|-------------------------------------------------|----------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------|
| 0                      | 19 864                                          | 24 258                                                   | 4 394                                                     | 24 240                                                     | 4 376                                                       |
| 10                     | 20 095                                          | 24 555                                                   | 4 460                                                     | 24 581                                                     | 4 486                                                       |
| 25                     | 20 424                                          | 22 700                                                   | 2 276                                                     | 23 245                                                     | 2 821                                                       |
| 40                     | 21 240                                          | 20 858                                                   | -382                                                      | 22 837                                                     | 1 597                                                       |

the cross section of the molecule yields a volume expansion of about 12 cm<sup>3</sup> mole<sup>-1</sup>. This estimate compares favorably with the observed values listed in Table 5 for several unimolecular decom-

positions in which large changes in the interaction with the solvent probably do not occur. Hamann (17) has reviewed a number of free-radical decompositions which have similar volumes of activation.

The transfer of charge from Cl to *t*-Bu will tend to make the Cl part expand due to the decreased nucleus-electron attraction and the *t*-Bu part contract due to the increased nucleus-electron attraction (18). The two effects will tend to compensate one another, and for lack of knowledge they are neglected.

The increased electrostatic interaction with the solvent when the transition state is formed causes a volume decrease. This might be expected to be similar to the volume decrease accompanying the formation of zwitter-ions of  $\alpha$ -amino acids



but probably somewhat smaller because the charges will not be so well separated in the transition state. According to density measurements of Cohn and others (19, 20a), the volumes of formation of zwitter-ions from the unionized amino acids are in the range -13 to -18 cm<sup>3</sup> mole<sup>-1</sup>.

If the charges are almost fully developed in the transition state for the solvolysis of *t*-butyl chloride, the expansion due to the stretching of the

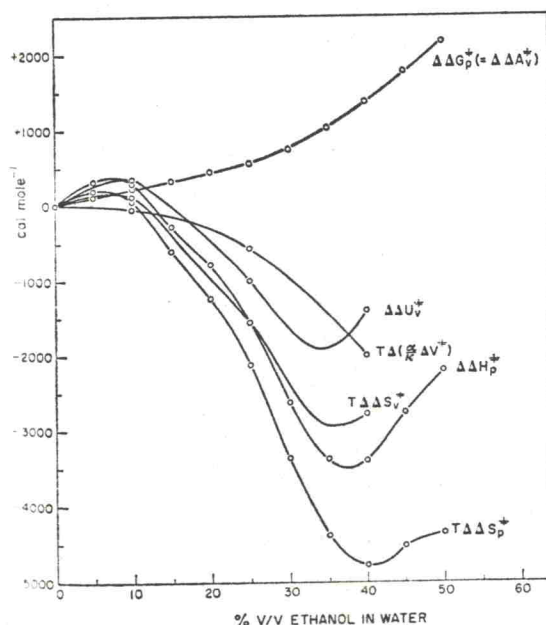


FIG. 4. Changes in the activation parameters for the solvolysis of *t*-butyl chloride with composition in ethanol-water at 0 °C.

and Hamann (9) in 0 °C which yield a  $-21 \text{ cm}^3 \text{ mole}^{-1}$ , and Laidlaw (10) at 30 °C, which by  $-22.2 \pm 0.9 \text{ cm}^3 \text{ mole}^{-1}$  cal reanalysis -20 and Virtanen (11) on volume for the in several organic and obtained values  $41.7 \text{ cm}^3 \text{ mole}^{-1}$ . Quite different, these with ours.

and entropy at con- Winstein and Fain- ince their enthalpies, they were adjusted of activation graph- e recently measured 2). The data in the used to obtain the entropy of activa- ons

$T\alpha\Delta V^\ddagger/\kappa$

$\alpha\Delta V^\ddagger/\kappa$ ,

st two columns of ivation parameters e plotted in Fig. 4.

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hat the solvolysis of two steps, the first of the halide and the of the *t*-butyl car- it. Presumably, the

-Cl<sup>δ-</sup>

tretched and partial the separating frag- te essentially to the ion (14, 15); (i) the substrate and (ii), the changes in the interac- substrate.

s (16) suggested that l by about 0.7 Å to d this multiplied by