

# The Pseudo Thermodynamics of Solvolysis. A Detailed Study of the Pressure and Temperature Dependence of Benzyl Chloride Solvolysis in *t*-Butyl Alcohol – Water Mixtures

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The pseudo first order rate constants for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol (*t*-BuOH) are reported at 40.00, 50.25, and 60.50 °C at various pressures up to 4084 atm. From these data the first temperature derivatives ( $\Delta H^*$  and  $\Delta S^*$ ), the first ( $\Delta V^*$ ) and second pressure derivatives,  $\partial\Delta V^*/\partial P$ , and the mixed second derivative,  $\partial\Delta V_0^*/\partial T$ , of the rate are evaluated. These activation parameters exhibit extremum behavior in the highly aqueous solvent region. This behavior is discussed in terms of solvent structure variation. The signs of the pressure dependence of  $\Delta H^*$  and  $\Delta S^*$  are shown to be consistent with those required by the Maxwell type relationships for classical thermodynamic systems.

Les constantes de vitesse du pseudo premier ordre pour la solvolysé du chlorure de benzyle dans l'alcool tertiobutyllique (*t*-BuOH) sont rapportées à 40.00, 50.25, et 60.50 °C pour différentes pressions supérieures à 4084 atm. A partir de ces données, les dérivées premières de la vitesse par rapport à la température ( $\Delta H^*$  et  $\Delta S^*$ ), ses dérivées première ( $\Delta V^*$ ) et seconde par rapport à la pression,  $\partial V^*/\partial P$ , et sa dérivée seconde  $\partial\Delta V_0^*/\partial T$  sont calculées. Ces paramètres d'activation montrent un comportement extrême dans la région des solvants fortement aqueux. Ce comportement est analysé en fonction de la variation de structure du solvant. On montre que les signes de  $\Delta H^*$  et  $\Delta S^*$  dépendant de la pression sont compatibles avec ceux requis par les relations du type relations de Maxwell pour des systèmes thermodynamiques classiques.

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## Introduction

In recent years a number of researchers (1–3) have investigated the behavior of the first derivative pseudo thermodynamic activation parameters. Their efforts have demonstrated that many interesting phenomena are concealed in free energy parameters by the compensatory behavior of enthalpy and entropy. More recently the extremum behavior exhibited by  $\Delta H^*$  and  $\Delta S^*$  in aqueous binary solvent mixtures has been observed for the volume,  $\Delta V^*$ , (4–6) and the heat capacity,  $\Delta C_p^*$ , (7) of activation. The particular sensitivity of  $\Delta C_p^*$ , the second derivative of the rate with respect to temperature, to variation of the binary solvent composition suggests that the parameter may be even more valuable than  $\Delta H^*$  or  $\Delta S^*$  for the investigation of solvent effects on reaction rates. This increased sensitivity of a second derivative parameter also prompts investigation of the second pressure derivative of the rate,  $\partial\Delta V^*/\partial P$ .

A major difficulty in understanding the solvent dependence of the various pseudo thermodynamic parameters has arisen because no single system has been examined exhaustively to obtain values

for all of the accessible activation parameters. Accordingly, it was decided to examine the solvolysis of benzyl chloride in *t*-butyl alcohol – water binary solvent mixtures with a view to determining  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta V^*$ ,  $\partial\Delta V^*/\partial P$ ,  $\partial\Delta V^*/\partial T$ ,  $\partial\Delta H^*/\partial P$ , and  $\partial\Delta S^*/\partial P$ . A summary of the relationship between the various derivatives is demonstrated in Fig. 1. The  $\Delta C_p^*$  value was not included in this study since the accurate determination of this parameter requires that the rate be measured at many more than the three temperatures used in this work.

The technique of dissecting the differential pseudo thermodynamic parameters of activation into their component initial and transition state parts has been previously employed (4, 8). In this study the enthalpy and volume of activation were so dissected by determining the partial molal enthalpies and volumes of solution of the initial state benzyl chloride as a function of binary solvent composition. Such dissections establish whether the initial state or transition state is primarily responsible for the observed behavior of the differential activation parameter.

The Maxwell relationships shown in eqs. 1 and