sign could be determined. It is apparent, from the results listed in Table 7, that the signs of $\partial\Delta H^*/\partial P$ and $\Delta V_0^* - T\partial\Delta V_0^*/\partial T$ are in agreement with eq. 20.

Although it is not presently justifiable to extract numerical values which would permit rigorous checks of the validity of eqs. 19 and 20 for pseudo thermodynamic parameters, the agreement of signs obtained in these complex second derivative relationships serves to establish further the credibility and reality of the mixed second derivative parameters obtained from exhaustive examination of the temperature and pressure dependence of the rate of this solvolytic reaction.

Conclusion

(1) The extremum behavior exhibited by the activation parameters, as a function of solvent composition, holds clues to our understanding of kinetic solvent effects. Explanation of these extrema requires knowledge of both the initial and transition state solvent dependences.

(2) The extrema observed in ΔH^*, ΔS^*, and ΔV^* are also present in the second derivative parameters. These latter exhibit more pronounced extremum behavior and, as in the study of ΔH^* and ΔS^* behavior, may further aid our comprehension of these systems.

(3) The analogous behavior of the activation parameters and non-kinetic properties of the solvent itself indicate that the extrema in the former are related to solvent structure.

(4) The validity of Maxwellian type relationships in this pseudo thermodynamic system supports the application of real state thermodynamics to kinetic systems.

(5) The evaluation of a third derivative of the rate, the temperature dependence of $\partial\Delta V^*/\partial P$ is at present premature. Figure 9 suggests that $\partial\Delta V^*/\partial P$ is temperature dependent, but this dependence is small. This demonstrates that, in spite of the extreme accuracy of the data, still greater reproducibility will be necessary to permit the determination of third derivative pseudo thermodynamic parameters.

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