ON THE PRESSURE DEPENDENCE OF REACTION RATES

H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne
Department of Chemistry, University of Calgary, Calgary, Alberta

Received March 8, 1966

ABSTRACT

The functional dependence of the rate constant for benzyl chloride solvolysis on pressure is investigated with a view to obtaining reliable values of the activation parameters. It is concluded that a second order polynomial is the best description of this system, reproducing the experimental data with a greater degree of precision than the other published functions. A method for determining the precision of the derivatives of the logarithmic rate is presented, and the pressure dependence of the activation volume is demonstrated. Various systems from the literature are analyzed to demonstrate the general applicability of the quadratic function.

INTRODUCTION

The pressure dependence of reaction rate has long been used to obtain the pseudothermodynamic parameter of activation, ΔV^*, the volume change on activation. The sign and numerical value of this parameter are clearly related to such important mechanistic phenomena as bond extension and solvent electrostriction during the activation process. Accordingly, considerable attention has been directed toward obtaining meaningful ΔV^* values for a number of solvolytic and displacement reactions in an attempt to further elucidate the mechanisms of these processes. The major problems faced in such determinations are twofold: firstly the determination of rate constants (k) as a function of pressure of sufficient precision to permit extraction of ΔV^* values with associated error limits that are small compared with the numerical magnitude of ΔV^* itself; and secondly the establishment of the *functional dependence* of the rate constant on pressure.

These problems are similar to those that for many years characterized the difficulties attendant upon the determination of activation enthalpy, ΔH^*. Here, the corresponding problems were those of accurate rate determinations as a function of temperature and the establishment of the functional dependence of rate constant on temperature. It was not until the postwar period that rate data of sufficient accuracy became available to permit detailed testing of various functional dependencies of rate on temperature. Such work led to the recognition of the reality of the ΔCp^* activation parameter, implying the nonlinear dependence of $\ln k$ on $1/T$, or alternatively, the temperature dependence of ΔH^* (1). Many of the analytical problems associated with the rate/pressure dependency are remarkably similar to those previously encountered in the rate/temperature relationship, as will be seen in subsequent sections of this paper.

Crucial to the whole problem of both rate/temperature and rate/pressure dependency is the determination of sufficiently accurate rate data. Although there inevitably will be continued scepticism as to whether the rate data obtained are, in fact, of sufficient accuracy to permit the refined analysis necessary to test various functional dependencies, it seems to us that at some stage a start must be made to obtain an objective technique for comparing the various functional forms. We believe that the rate data on the solvolysis of benzyl chloride in ethanol–water mixtures as a function of pressure analyzed in this paper are of sufficient accuracy. The *in situ* conductimetric technique used to follow the rate of the reaction as a function of pressure is very similar to the methods used to

Canadian Journal of Chemistry. Volume 44 (1966)

obtain highly accurate rate/temperature data. We have also applied our analytical methods to a number of other sets of rate/pressure data available in the literature. Although the precision of these data may well not be sufficient to justify the refined level of analysis applied, the form of analysis used in a number of the cases cited has been the basis of protracted argument in the literature (2, pp. 98–99; 3; 4). The application of our analytical comparison to these cases therefore serves to highlight the crucial factors involved in the formulation of the rate/pressure dependency.

BENZYL CHLORIDE SOLVOLYSIS (RATE DATA)

The rate of solvolysis of benzyl chloride in various water–ethanol mixtures has been studied as a function of pressure up to 4 000 atm at 50.25 °C (5). The rate data as a function of pressure and solvent composition is reproduced in Table I. The most crucial aspect of this data as far as the purpose of this paper is concerned is the confidence that can be placed in the error limits claimed for each rate constant. The *in situ* conductimetric technique used eliminates many of the sampling and timing errors that are characteristic of aliquot sampling techniques.

TABLE I

Rate constants and activation parameters for the solvolysis of benzyl chloride in aqueous ethanol at 50.25 °C

Pressure (atm)	$10^5 \times k$ (s^{-1}) for mole fraction ethanol				
	0.000	0.100	0.200	0.300	0.400
1	23.1 ±0.4	6.690±0.007	1.93±0.01	0.80±0.01	0.459±0.007
341	24.42±0.02	8.47 ±0.01	2.46±0.01	1.06±0.01	
681	30.0 ±0.2	10.25 ±0.02	3.02±0.07	1.29±0.01	0.68 ±0.03
1 362	39.3 ±0.3	13.68 ±0.01	4.64±0.01	2.04±0.03	1.041±0.002
2 723		21. ±2.	7.7 ±0.2	3.00±0.02	1.81 ±0.02
4 084					2.6 ±0.2
ΔV_0^* (ml/mole)	−8. ±1.	−17. ±1.	−20.3±0.2	−22.9±0.2	−17.9±0.9
$10^3 \times (\partial \Delta V^*/\partial p)_T$ (ml/atm mole)	−4. ±1.	+4. ±1.	+4.9±0.3	+7.3±0.1	+3.2±0.6

The considerable variation in the percentage size of the uncertainty claimed for each rate results from the concommitant variation in the experimental difficulties encountered as solvent and pressure are varied. The uncertainty tends to be larger at higher pressures where rates are faster and pressure control more difficult.[1] Similarly in more aqueous media the rates are also faster, resulting in a shorter reaction period available for study after pressure and temperature equilibration in the pressure vessel has been attained. The combination of all of these factors results in considerable variation of the uncertainty limits associated with each rate reported. Because of the crucial nature of the rate accuracy factor in such a study, however, it would be completely unjustifiable to report a single averaged uncertainty for all of the rate values.

The actual uncertainties reported in Table I are obtained from a minimum of two independent rate determinations and in many cases from three or four independent determinations.

---

[1] *The automatic pressure-regulating device used in this study (5) enabled the pressure to be controlled to ±14 atm (200 psig).*