additional, secondary, electrostatic solvation which may occur is not observable from equilibrium measurements of the type reported here. Nitrobenzene is considerably less basic than the ethers.[29] Thus it is questionable whether it is capable of coordination at all; if so, it undoubtedly does so only with the $H_9O_4^+$. Since this cannot reasonably account for the large values of *n* in the nitrobenzene systems, it seems likely that here we are observing a more general electrostatic interaction between the polar molecules and the ions as well as (perhaps) coordinate solvation. These two types of binding are presumably indistinguishable (by our techniques) for nitrobenzene. Whether the differences between nitrobenzene and ethers are due to the considerably larger dipole moment or lesser basicity of nitrobenzene, geometry effects, dissociated ions *vs.* ion pairs, anion solvation, or a combination of these, or other effects, is not known at present; further speculation would seem fruitless in view of the lack of structural information for these solvates.

The Effect of Pressure on the Rate of Solvolysis of Benzyl Chloride in Aqueous Ethanol

J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw

Contribution from the Department of Chemistry, University of Alberta, Calgary, Alberta, Canada. *Received November 18, 1965*

Abstract: The high-pressure apparatus and associated conductometric technique for following rates of solvolysis of alkyl halides in ethanol–water mixtures as a function of pressure are described. Results of the redetermination of ΔV_0^* for *t*-butyl chloride in 80% aqueous ethanol are presented to establish the precision and accuracy of the method. The dependence of ΔV_0^* on the composition of the ethanol–water medium for solvolysis of benzyl chloride is reported. ΔV_0^* for this system passes through an extremum at approximately 0.3 mole fraction of ethanol.

The influence of solvent on the kinetics of reactions in solution has been the subject of intensive study for the past 4 decades. Over this period the progressive refinement of the arguments and rationalizations of observed effects has left little doubt that the major impediment to a detailed understanding of the phenomenon is the lack of a definitive description of the liquid state of the solvent system. As a result of these limitations the explanations offered for solvent effects on rate processes have been largely of the empirical type. Relationships between rate and expressions involving bulk dielectric constant[1-6] have been most commonly employed together with linear free energy relationships of the *mY* type as proposed by Winstein, *et al.*[7] The principal objection to the use of these parameters has been that they reflect the bulk properties of the solvent medium, but neglect any specific type of substrate–solvent interaction that may be of more than passing significance in determining solvent effects on the rate process. Recently, spectroscopically determined solvent parameters of the type proposed by Kosower[8] (*Z* values) appear to take better account of such specific interactions, but even in these cases the rate relationships with such parameters are essentially empirical in form.

Notwithstanding the apparent lack of understanding of the specific nature of the substrate–solvent interaction in single component solvent systems, there has recently been a considerable revival of interest in the effect of varying the composition of binary solvent media on the various kinetically measurable rate parameters, ΔH^*, ΔS^*, and ΔC_p^*.[9-13] These pseudo-thermodynamic parameters exhibit an extremum behavior as a function of solvent composition that is not manifest in the directly measurable log *k* or ΔF^*. Compensatory effects of ΔH^* and ΔS^* ($\Delta F^* = \Delta H^* - T\Delta S^*$) are generally accepted as the reason for this phenomenon.

The observed extremum behavior of these kinetic parameters in binary solvent systems has been ascribed to a specific interaction between the reacting substrate and the binary solvent environment. Until recently, however, there was no experimental evidence to indicate whether the initial or transition state, or both, of the reacting substrate is primarily influenced by these specific solvent effects since the various Δ parameters measure the *difference* between the initial and transition states. This difference could vary as a result of changes in either the initial or transition state or changes in both. Recently, however, Arnett and co-workers[14,15] have measured "instantaneous" heats of solution of reacting

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(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

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(8) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(9) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); **79**, 1597, 1602, 5937 (1957).

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(13) J. B. Hyne, *et al.*, *J. Am. Chem. Soc.*, (a) **85**, 3650 (1963); (b) **84**, 2914 (1962); (c) **82**, 5129 (1960).

(14) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, **85**, 1350 (1963).

(15) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

substrates in binary solvent mixtures, and thus have a measure of variation of the initial state end of the enthalpy difference. With this information available, Arnett, *et al.*, have shown that for a variety of reacting substrates in binary solvent mixtures the extremum behavior of ΔH^* can result from changes in substrate–solvent interaction at *either* the initial *or* transition state end of the differential, *or* both.

The apparent initial success of these attempts to interpret the behavior of ΔH^* with solvent composition variation in terms of specific solvent effects has led us to an examination of the solvent composition behavior of the one remaining, readily accessible, pseudo-thermodynamic parameter, ΔV^*, the volume change on activation. It is clear that if there is a significant change in substrate–solvent interaction through a series of solvents, either at the initial state or transition state end of the differential, such changes should be reflected in the volume change on activation. As in the case of ΔH^*, which results from the temperature dependence of log k, ΔV^* cannot be measured directly, but results from the pressure dependence of reaction rate. Since we are interested in the *variation* of this pressure dependence with the solvent composition, the required precision of measurement of the rate at various pressures is somewhat higher than has been previously common. In this paper we describe a precision conductometric method for measuring the rate of solvolysis of alkyl halides as a function of both binary solvent composition and pressure. The method is checked against the previously reported rate constants for *t*-butyl chloride in 80% ethanol–water, and the solvent composition dependence of ΔV_0^* for the solvolysis of benzyl chloride in ethanol–water mixtures is reported. In the benzyl chloride case, ΔV_0^* is found to exhibit an extremum as solvent composition is varied.

Experimental Section

High-Pressure Apparatus. A schematic diagram of the hydrostatic system is presented in Figure 1a. The high-pressure vessel is a modified version of the AEM series manufactured by Autoclave Engineers, Inc. (Erie, Pa.). It is equipped with four Covar leads which pass through the cover and are insulated from it by porcelain. A brass mounting fitted to the outside of the cover holds the BNC connectors which are connected to the leads. Pressurization of the reactor is accomplished by means of an air-driven pump manufactured by Autoclave Engineers, Inc. The pressurizing liquid is Blackhawk hydraulic fluid.

The pressure was measured by a 16-in. dial Bourdon tube gauge manufactured by Heise-Bourdon Tube Co. (Newark, N. J.) and calibrated in units of 3.402 atm. Automatic pressure control was accomplished by use of a micro switching mechanism inserted in the face plate of the gauge. An auxiliary pointer, equipped with a very light side arm, was preset to the desired pressure reading. When this pressure was reached in the system, the gauge needle lifted the side arm causing a break in the control circuit and closure of a solenoid valve in the air supply line. When the pressure fell, contact was remade and pressurization resumed. This method enabled the pressure to be controlled to better than ±15 atm over the entire range above atmospheric. It may be noted that a delicate balance of the watch spring system in the switching device was necessary to avoid distortion of the gauge reading.

Conductivity Apparatus. Twin high-pressure conductivity cells of the type shown in Figure 1b were used as reaction vessels, permitting two simultaneous kinetic determinations to be made. These were suspended in the pressurizing fluid of the hydrostatic vessel, and the platinum electrode terminals were connected to the Covar leads. Each compartment of the cell consisted of an 8-ml capacity bulb with two platinum bead electrodes sealed into the wall. The value of the cell constant was not required in the Guggenheim method of first-order rate analysis[16] employed. Pressure was transmitted to the cell contents by a 0.25-in. Teflon piston operating in a precision bore glass tube attached to each cell compartment. The pressure difference across the glass wall was therefore zero. Care had to be exercised in filling the cells so that no air bubbles remained in the cell compartments, and working solutions were degassed before use. Leakage past the Teflon piston was not a problem; the only operational problem arising in the system was the fracturing of the platinum to glass seals after several pressurizations, particularly at pressures above 1364 atm. This behavior, although inconvenient, was tolerated, and the cells simply were replaced at frequent intervals. The ac conductivity bridge was of conventional design, but specially constructed from high-precision components by Mr. T. Clement of this department. A sensitivity of 1 ohm in 80,000 was attainable.

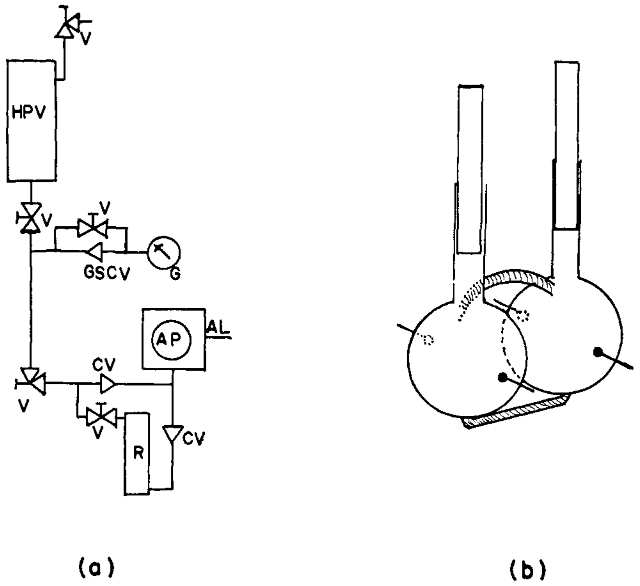

Figure 1. High-pressure apparatus. (a) Schematic diagram of the hydrostatic system: AL, air line; AP, air pump; CV, check valve; G, gauge; GSCV, gauge surge check valve; HPV, high pressure vessel; R, reservoir; V, valve. (b) High-pressure conductivity cell.

Temperature Control. Because of the temperature sensitivity of both conductance and rate, accurate control of this parameter is of crucial importance in obtaining precision conductometric rate constants. While for rate studies at atmospheric pressure such control can be conveniently accomplished by direct immersion of the conductance cell in a precision thermostat, the presence of the pressure vessel between the thermostating fluid and the reaction cell necessitated a careful check of temperature control in this work. In addition, heating effects due to pressurization further complicate the matter of temperature control.

A 50-gal oil thermostat capable of ±0.005° control at 50° in an air-conditioned room at 22° ambient temperature was used throughout this work. The complete pressure vessel assembly was immersed in the thermostat and could be raised by a chain hoist sufficiently to expose the removable head for cell loading. The vessel itself was never removed from the thermostating fluid. In order to determine the time interval required for thermal equilibration after loading and pressurizing, the following procedures were used.

A special cell containing water at 0° and equipped with a thermocouple was used as a "dummy" in the pressure vessel, and normal loading techniques followed. After 30 min no temperature difference between the cell contents and thermostat fluid at 50° could be detected. As an additional check of the thermal equilibration interval, a conductivity cell of the type used in the rate studies, but containing an aqueous solution of 5×10^{-4} mole/l. of KCl at 0°, was loaded into the pressure vessel in the normal manner. Resistance measurements were then taken at 1-min intervals. It was found that after 30 min the resistance changed by only 2 to 3 ohms between readings, indicating that the cell temperature was very close to equilibrium.

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(16) E. A. Guggenheim, *Phil. Mag.*, (7) **2**, 538 (1926).

Table I. Rate Constants for the Solvolysis of *t*-BuCl in 80% (v/v) Aqueous Ethanol at 30.00°

Pressure, atm	10^5k, sec^{-1} This work	10^5k, sec^{-1} Ref 19
1	1.90 ± 0.03	1.7 ± 0.5
681	3.14 ± 0.07	2.7 ± 0.7
1362	4.92 ± 0.05	4 ± 1
2042	6.7 ± 0.3	5 ± 2
ΔV_0^*,[a] ml/mole	-22.2 ± 0.9	-21 ± 4

[a] Throughout this series of papers, ΔV_0^* will be used to refer to the volume of activation evaluated at atmospheric pressure, while ΔV^* will refer to an activation volume of unspecified pressure.

Materials. Singly distilled water was passed through Illco-Way deionizing resin. It was then distilled in a Pyrex apparatus from which atmospheric carbon dioxide was excluded, and stored in polyethylene containers.

Standard hydrochloric acid was prepared by the method of Hulett and Bonner.[17]

The ethanol used was Reliance Chemicals absolute ethanol. It was dried over magnesium turnings by the method of Lund and Bjerrum.[18]

Eastman White Label *t*-butyl chloride was used without further purification.

Eastman White Label benzyl chloride was distilled in small quantities at 1×10^{-3} mm, as needed.

Kinetics. The mixtures of ethanol and water were prepared by weight to ±0.0002 mole fraction. Solutions of approximately 5×10^{-4} mole/l. of alkyl halide in the desired solvents were prepared by weight. These were filtered into a vial containing a stopcock and standard taper joint enabling the solutions to be degassed. The vial was then closed with a rubber septum, and the solutions were degassed by twice freezing, evacuating to a pressure of 10^{-3} mm, and thawing. They were then stored under vacuum in an ice–water bath.

New conductivity cells were initially cleaned with hot concentrated nitric acid and distilled water. Prior to a kinetic run each cell was aged with a solution of 5×10^{-4} mole/l. of HCl in the desired solvent for a minimum of 12 hr at the pressure and temperature to be used. The cell was then removed from the pressure vessel, emptied, and rinsed three times with acetone and three times with doubly distilled water (as above).

The vacuum in the vial containing the reaction mixture was released, after thorough agitation, and the desired amount of solution extracted through the rubber septum into a syringe. The reaction cell was rinsed twice with the solution and then filled to the top. The Teflon piston was inserted displacing some of the solution. This method prevented the entrapment of air bubbles. The cell was then placed in the high-pressure vessel which was lowered into the thermostat and connected to the pressurizing system. The vessel was brought up to the desired pressure, and sufficient time was allowed for thermal equilibrium to occur (30 min for those runs having half-lives of less than 2 hr and 60 min for the longer runs).

Twenty resistance measurements were taken at equally spaced intervals over approximately 1 half-life of the reaction. After 2 half-lives had elapsed a second set of 20 measurements was made at the same intervals.

Results

Rates. The conductance data was analyzed, according to the method of Guggenheim,[16] by eq 1 where Δt is an interval of about 2 half-lives of the reaction.

$$\ln\left(\frac{1}{R_{t+\Delta t}} - \frac{1}{R_t}\right) = -kt + \ln\left(\frac{1}{R_\infty} - \frac{1}{R_0}\right)(1 - e^{-k\Delta t}) \quad (1)$$

The method of least squares was used to solve eq 1 for *k*.

Table II. Rate Constants and Activation Parameters for the Solvolysis of Benzyl Chloride in Aqueous Ethanol at 50.25°

Pressure, atm	10^5k, sec^{-1} 0.000[a]	0.100[a]	0.200[a]	0.300[a]	0.400[a]
1	23.1 ± 0.4	6.690 ± 0.007	1.93 ± 0.01	0.80 ± 0.1	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
1362	39.3 ± 0.3	13.68 ± 0.01	4.64 ± 0.01	2.04 ± 0.03	1.041 ± 0.002
2723		21 ± 2	7.7 ± 0.2	3.00 ± 0.02	1.81 ± 0.02
4084					2.6 ± 0.2
ΔV_0^*, ml/mole	-8 ± 1	-17 ± 1	-20.3 ± 0.2	-22.9 ± 0.2	-17.9 ± 0.9
$10^3(\partial\Delta V^*/\partial p)_T$, ml/atm mole	-3 ± 1	$+4 \pm 1$	$+4.9 \pm 0.3$	$+7.2 \pm 0.1$	$+3.2 \pm 0.6$

[a] Mole fraction of ethanol.

***t*-Butyl Chloride.** In order to check the apparatus and techniques, the rate of solvolysis of *t*-butyl chloride in 80% (v/v) aqueous ethanol at 30.00° as a function of pressure was studied. This system was studied previously by Buchanan and Hamann.[19] Our results for the first-order rate constant, together with those interpolated from the data of these authors, are given in Table I. The errors reported for our data are the average deviations of simultaneous, duplicate runs, whereas those for the interpolated data of Buchanan and Hamann are the 30% errors modestly claimed by Hamann.[20]

Benzyl Chloride. The first-order rate constants for the solvolysis of benzyl chloride in aqueous ethanol as a function of pressure are given in Table II. Most of these contants are the average of duplicate, simultaneous runs, while some are the average of three, nonsimultaneous determinations. The average deviations are also reported in Table II.

Activation Volumes. It was found that our data for the solvolysis of benzyl chloride are reliably described by eq 2 (see Appendix I).

$$\ln k = A + Bp + Cp^2 \quad (2)$$

Hence

$$\Delta V_0^* = -RTB \quad (3)$$

The parameters of eq 2 were calculated by the method of least squares, and those for benzyl chloride are pre-

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(17) G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.*, **31**, 390 (1909).

(18) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., Ltd., London, 1961, p 167 ff.

(19) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).

(20) S. D. Hamann, private communication.

sented in Table III, while the activation volumes at atmospheric pressure are given in Table II. It may be noted that the pressure dependence of the activation volume, as calculated by eq 2, is

$$\left(\frac{\partial \Delta V^*}{\partial p}\right)_T = -2RTC \qquad (4)$$

The values of this activation parameter are also given in Table II. All error limits shown for the activation parameters were calculated by the method described in Appendix I.

Table III. The Values of the Parameters of Eq 2

Mole fraction of ethanol	A	10^5B, atm^{-1}	10^8C, atm^{-2}
0.000	-8.39 ± 0.02	31 ± 4	$+6 \pm 2$
0.100	-9.599 ± 0.002	65 ± 3	-9 ± 2
0.200	-10.864 ± 0.005	76.4 ± 0.9	-9.3 ± 0.4
0.300	-11.744 ± 0.007	86.1 ± 0.7	-13.6 ± 0.2
0.400	-12.30 ± 0.03	68 ± 3	-6 ± 1

Discussion

Solvolysis of *t*-Butyl Chloride. The main purpose of studying the pressure dependence of rate of solvolysis of *t*-butyl chloride in 80% (v/v) ethanol–water was to compare the results obtainable using the apparatus described with those previously published by Buchanan and Hamann.[19] This comparison is presented in Table I. Our results are well within the error range reported by these authors;[20] of greater significance is the fact that the higher precision of our rate determination permits the evaluation of an activation parameter with considerably smaller uncertainty. This increase in confidence is necessary for the meaningful study of ΔV_0^* variation with solvent composition, and essential if the pressure dependence of ΔV_0^* is a desired parameter.

Solvolysis of Benzyl Chloride. The values of ΔV_0^* for benzyl chloride solvolysis in ethanol–water mixtures shown in Table II are all negative. This observation is consistent with previous claims that the major contribution to changes in volume on activation for ionogenic reactions is in the structure of the immediate solvent environment rather than in the substrate itself.[19,21]

The dependence of ΔV_0^* on solvent composition is characterized by behavior of the type previously reported[13b] for the behavior of ΔH^* and ΔS^*. A comparative presentation of the behavior of these three activation parameters is demonstrated in Figure 2, the ΔH^* and ΔS^* values having been calculated from the data of ref 13b. In a recent report, Whalley and coworkers[22] comment on the apparent compensatory behavior between enthalpy and entropy or volume changes on activation. In their interpretation of the effect of pressure on the hydrolysis of methyl acetate and ethylene oxide in acetone–water mixtures, these authors state that for these systems "the existence of the minimum is therefore best considered as a trivial fact, not related to mechanism except insofar as changes in $T\alpha\Delta V^*/\kappa$ are related to mechanism."[22] Supporting evidence for this statement consists primarily of the observation that no extremum behavior is noted in the activation energy at constant volume, $\Delta U_v^* = \Delta H_p^* - T\alpha\Delta V^*/\kappa$. Whalley and co-workers further state that most of the change in the term $T\alpha\Delta V^*/\kappa$, which results in compensation of the extremum behavior of ΔH_p^*, is "due to changes in the thermal expansivity α of the solvent. . .[while] changes of the volume of activation contribute to a smaller extent, and changes of the compressibility [κ] are of little consequence."

The results plotted in Figure 2 clearly establish that the compensating extremum behavior characteristic of ΔH^* and ΔS^* is also a feature of ΔH^* and ΔV_0^*. Consequently at least some scepticism arises regarding the "trivial" nature of such extrema although the possible semantic nature of any disagreement on this point must not be overlooked.

One immediately obvious feature of the ΔV_0^* dependence on solvent composition is the higher ethanol concentration at which the extremum occurs compared with ΔH^* and ΔS^*. If the fundamental reason for the existence of these extrema is the same for all three activation parameters, it must be concluded that the factors leading to the extremum in ΔV_0^* have a different dependence on solvent composition from those responsible for the extremum in ΔH^* and ΔS^*. The existence of such a situation is not hard to envision since ΔV_0^* behavior is probably *more directly* related to solvent structure than either ΔH^* or ΔS^*. It is interesting to note at this point that the excess thermodynamic parameters of mixing of ethanol with water[23] show extremum behavior between 0.2 and 0.4 mole fraction of ethanol rather than at the lower ethanol concentration characteristic of ΔH^* and ΔS^*.

Turning to the question of the source of the extremum in ΔV_0^*, the ever present question of "which end of the differential is responsible" arises. Like ΔH^* and ΔS^*, ΔV_0^* is a difference between the partial molal volume of the kinetically effective initial state (including solute and associated solvent) and that of the transition state. As the solvent composition is varied, either or both of these volumes can be altered, leading to variation of ΔV_0^*. The recent, elegant work of Arnett and co-workers[14,15] has been directed toward answering this question as it relates to the behavior of ΔH^*. As yet, no similar breakdown of ΔV_0^* for the benzyl chloride system under study here is possible since the partial molal volume of benzyl chloride in the various solvent mixtures is not available. Such work is currently underway in these laboratories on various systems. In this regard, however, it is interesting to note the work of Bateman on the apparent molal volume of barium chloride in ethanol–water mixtures,[24] which shows the molal volume to have a maximum value at 0.3 mole fraction of ethanol. If the crude assumption is made that barium chloride, as an ionic species, bears some resemblance to the transition state of benzyl chloride solvolysis, then the suggestion may be advanced that

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(21) (a) H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **50**, 1188 (1954); (b) A. H. Ewald and S. D. Hamann, *Australian J. Chem.*, **9**, 54 (1956); (c) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955); (d) S. D. Hamann and W. Strauss, *Discussions Faraday Soc.*, **22**, 70, (1956).

(22) B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *Trans. Faraday Soc.*, **61**, 517 (1965).

(23) A. G. Mitchell and W. F. K. Wynne-Jones, *Discussions Faraday Soc.*, **15**, 161, (1953).

(24) R. L. Bateman, *J. Am. Chem. Soc.*, **74**, 5516 (1952).

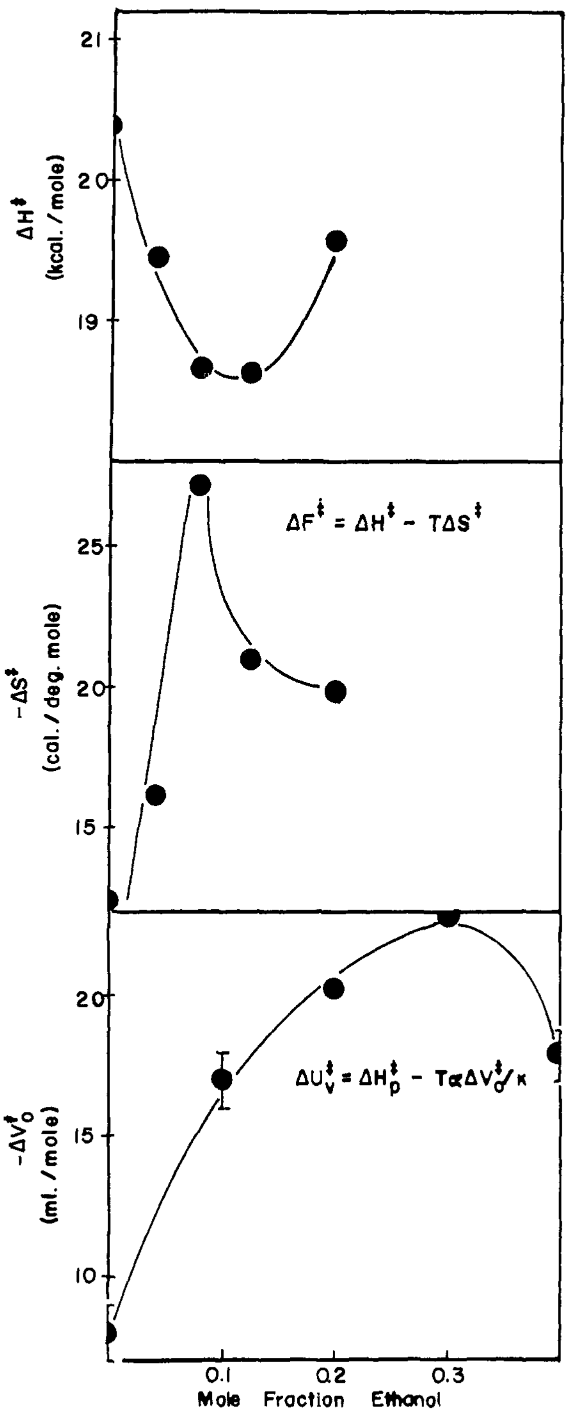

Figure 2. Solvent composition dependence of activation parameters for benzyl chloride solvolysis in ethanol–water mixtures.

the extremum behavior of ΔV_0^* may be due to changes in transition state solvation.

Pressure Dependence of ΔV^*. The precision of previous rate determinations as a function of pressure usually has been inadequate to permit evaluation of the pressure dependence of ΔV^*. In many respects the problems of determining $(\partial \Delta V^*/\partial p)_T$ are similar to those for $(\partial \Delta H^*/\partial T)_p$ or ΔC_p^*. Both are second derivatives of rate with respect to environmental variables, and are responsile for the nonlinearity of the simple van't Hoff type plots of log k variation. Use of the quadratic function (eq 2) permits direct evaluation of $(\partial \Delta V^*/\partial p)_T$, and the error analysis described in the Appendix provides a measure of confidence for the values obtained. The values of $(\partial \Delta V^*/\partial p)_T$ shown in Table II, together with the corresponding error limits, leave little doubt as to the reality of this additional activation parameter. As in the case of ΔC_p^* for benzyl chloride solvolysis in ethanol–water, calculated from ref 13b, $(\partial \Delta V^*/\partial p)_T$ appears to show extremum behavior. It would be premature at this stage to attempt to give a physical picture accounting for this term, but it appears that modern kinetic techniques are capable of extending the range of measurable activation parameters to include this additional term.

Acknowledgments. Financial assistance by the National Research Council of Canada to H. S. G. is gratefully acknowledged. The authors wish to thank the staff of the University of Alberta, Calgary, Computing Centre, for writing the FORTRAN programs used in this study.

Appendix I

The question of obtaining a volume of activation from a set of rate constants at various pressures is one which has not been answered unambiguously. It is known that the relation between the activation volume and the pressure dependence of the rate constant is given by eq 5.[25] The difficulty lies in determining the func-

$$\Delta V^* = -RT(\partial \ln k/\partial p)_T \qquad (5)$$

tional dependence of ln k upon p so that $(\partial \ln k/\partial p)_T$ can be evaluated. Since we are interested in the variation of ΔV^* for reactions in solution as the composition of the binary solvent medium is changed, we must be concerned with obtaining as reliable a set of activation volumes and precision measurements as our data permit. This position has led us to a study of various functional representations of the dependence of k upon p.

Walling and Peisach,[26] Benson and Berson,[27] Burris and Laidler,[28] and Whalley, *et al.*,[29] have all used different methods for extracting the value of this derivative. We have examined each of these in turn and have found that the quadratic function (eq 2) best represents our data. The quantitative comparison of these various methods will be published elsewhere.

Having established the functional dependence of the rate of benzyl chloride solvolysis on pressure, the next step is to establish the precision of the derivatives. This is readily accomplished by determining the maximum deviations of the constants in eq 2. These in turn are conveniently determined by differentiation.[30] The least-squares functional forms of these constants were differentiated, and the values of dA, dB, and dC were calculated using an IBM 1620 computer. The average deviation of the rate constants were used for the dk_i's, and the pressure fluctuation limits were used for the dp_j's.

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[25] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 31, 875 (1935).

[26] C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

[27] S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

[28] C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, 51, 1497 (1955).

[29] B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *ibid.*, 61, 517 (1965); E. Whalley, *Advan. Phys. Org. Chem.*, 2, 100 (1964). Note that these references contain an error in the method of extracting the pressure dependence of ln k. The corrected version, as used here, is given in B. T. Baliga and E. Whalley, *Can. J. Chem.*, 43, 2453 (1965).

[30] F. Daniels, *et al.*, "Experimental Physical Chemistry," 5th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 326.