

ON THE PRESSURE DEPENDENCE OF REACTION RATES

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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 pseudo-thermodynamic 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

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 concomitant 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.

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

ANALYTICAL FUNCTIONS AND THEIR SIGNIFICANCE

Theoretical Considerations

No strictly theoretical, analytical function describing the pressure dependence of reaction rate is available. The usual differential form of the dependence used is that given by Evans and Polanyi (6),

$$[1] \quad \Delta V^* = -RT(\partial \ln k / \partial p)_T,$$

but the question immediately arises as to whether ΔV^* is pressure independent or not. Precisely the same question arises for the temperature dependence of rate where ΔH^* can be written

$$[2] \quad \Delta H^* = -RT(\partial \ln k / \partial \left(\frac{1}{T}\right))_p.$$

If the pseudo-thermodynamic ΔH^* parameter has the same form as the real thermodynamic ΔH , then it is not temperature independent, since there is a non-zero value of ΔC_p^* . In an exactly similar manner ΔV^* may be expected to be pressure dependent according to eq. [3]

$$[3] \quad (\partial \Delta V^* / \partial p)_T = -V_0^* \kappa^* \exp(-\kappa^* p) + V_0^g \kappa^g \exp(-\kappa^g p),$$

where the first term on the right-hand side refers to the transition state with V_0^* being the partial molal volume of the transition state at some reference pressure and κ the compressibility; the second term on the right-hand side applies similarly to the initial state. Equation [3] is unusable as an analytical function for treating experimental rate data, since the partial molal isothermal compressibilities (κ 's) cannot be determined in reacting systems.

While, therefore, there is good reason to believe that the functional dependence of rate on pressure is at least of second order with respect to pressure (just as the dependence of rate on temperature is second order in temperature), there is no theoretically derivable form of the functional dependence which has practical utility.

Two further factors must be considered as possible contributors to the pressure dependence of rate: concentration effects and viscosity effects. In solvolytic reactions of the benzyl chloride type considered here the reaction is between the molecular species of the solvent environment and the dissolved substrate. Accordingly, if the volume of the initial and transition states is considered to be the volume of the substrate *plus* its immediate solvation shell in both states the effect of pressure on "concentration" is included in the volume of the two states as so defined. The viscosity effect would not be expected to become a major contributor until the viscosity of the system increased to a point where the diffusion rate of the reacting species was significantly reduced. This requires very high pressures as has been shown by Hamann (7) where for bimolecular reactions the rate dependence on pressure actually changes sign from positive to negative at very high pressures. Again, however, in solvolyses reactions, diffusion together of the reacting species is not an important factor, since the reacting substrate is always in immediate contact with the reactant solvent.

The Functions

In the absence of a strictly based theoretical functional form of practical utility for expressing the dependence of rate on pressure, four basic semiempirical functions have been employed. It is the purpose of this paper to examine these relations between rate

and pressure from the standpoint of their utility and ability to reproduce the experimentally observed dependencies and not from the theoretical viewpoint. However, comments will be made when appropriate about the physical significance of the relationships. The first of these relationships assumes that the dependence of the logarithm of the rate constant on pressure is linear (8) (eqs. [4] and [5]). This treatment regards the activation volume as being pressure independent, and consequently neglects a possible additional activation parameter $-(\partial \Delta V^*/\partial p)_T$. The second type of function is a power series in p , usually of second order (9), which allows for the pressure dependence of the activation volume (eqs. [6] and [7]). Benson and Berson (4) have used a modified form of the Tait equation (10) to calculate both the volume of activation and the change in compressibility (eq. [8]).

Whalley has plotted the average slope of any increment of the $\ln k$ vs. p curve against the average pressure of that increment² (11; 2, p. 100). Extrapolation to an average pressure of zero gives an intercept which can be taken as equalling $(\partial \ln k/\partial p)_{T,p=0}$. Such a function is given in eq. [9] in which linearity of the incremental function is assumed.

In this study we considered each of these functions in turn, using the forms shown in eqs. [4] through [9]. Here k_0 is the rate constant at atmospheric pressure, and k_{n+1} and k_n are rate constants at adjacent pressures. Equation [5] is identical to eq. [4] except that, in the former, the curve is forced to pass through the experimental $\ln k_0$. Equations [6] and [7] also differ only in the forced intercept treatment.

$$[4] \quad \ln k = A + Bp$$

$$[5] \quad \ln k = \ln k_0 + Bp$$

$$[6] \quad \ln k = A + Bp + Cp^2$$

$$[7] \quad \ln k = \ln k_0 + Bp + Cp^2$$

$$[8] \quad \ln(k/k_0)/p = A + Bp^{0.523}$$

$$[9] \quad \ln(k_{n+1}/k_n)/(p_{n+1} - p_n) = A + B(p_{n+1} + p_n)/2$$

TEST OF BENZYL CHLORIDE SYSTEM

Using our experimental data (5) for the solvolysis of benzyl chloride in water and in mixtures of ethanol and water (Table I), we calculated the various constants of eqs. [4] through [9] by the method of least squares using an IBM 1620 computer. A representative set of these constants is presented in Table II. From these we obtained the values of the activation volume which are presented in Table III. The value at atmospheric pressure is reported for those functions which take account of the pressure dependence of ΔV^* .

Our interest lies in the variation of ΔV^* with solvent composition. This dependence is shown in Fig. 1. The values of ΔV^* obtained from functions [6] and [7] are identical for all solvents except pure water, and the difference at this one point is probably within the experimental error. It appears that utilization of the experimental intercept introduces no significant error. The values from functions [4] and [5], which also differ only with regard to the forced intercept treatment, do not agree so well. However, the differences are less than 2 ml/mole. It may be noted that the ΔV^* 's from function [9] agree

²Note that refs. 11 and 2, p. 100 contain an error in the statement of the method of extracting the pressure dependence of $\ln k$. The corrected version, as used here, is given in ref. 12.

TABLE II
 The functional constants for 0.3 mole fraction ethanol

Function	Constants		
	A	B	C
[4]	-11.620	$4.779 \times 10^{-4} \text{ atm}^{-1}$	
[5]		$5.379 \times 10^{-4} \text{ atm}^{-1}$	
[6]	-11.743	$8.615 \times 10^{-4} \text{ atm}^{-1}$	$-1.366 \times 10^{-7} \text{ atm}^{-2}$
[7]		$8.503 \times 10^{-4} \text{ atm}^{-1}$	$-1.334 \times 10^{-7} \text{ atm}^{-2}$
[8]	$9.742 \times 10^{-4} \text{ atm}^{-1}$	$-5.155 \times 10^{-7} \text{ atm}^{-1.523}$	
[9]	$8.284 \times 10^{-4} \text{ atm}^{-1}$	$-2.544 \times 10^{-7} \text{ atm}^{-2}$	

 TABLE III
 Volumes of activation for benzyl chloride solvolysis at 50.25 °C in aqueous ethanol†

Mole fraction ethanol	ΔV^* (ml/mole) for function					
	[4]	[5]	[6]	[7]	[8]	[9]
0.000	-10.9	-10.0	-8.3	-7.2	-0.4	-7.0
0.100	-10.8	-12.0	-17.0	-17.6	-21.9	-18.0
0.200	-13.4	-14.4	-20.3	-20.0	-21.6	-19.6
0.300	-12.7	-14.3	-22.9	-22.6	-25.9	-22.0
0.400	-11.3	-12.3	-17.6	-17.7	-19.0	-17.7

†The values reported for functions [6], [7], [8], and [9] are those evaluated at atmospheric pressure.

well with those from [6] and [7]. This is not surprising since all three allow for the pressure dependence of ΔV^* , i.e. $(\partial \Delta V^* / \partial p)_T \neq 0$. For this study we consequently can restrict further consideration to eqs. [4], [6], [8], and [9].

It is readily apparent that the general shapes of the curves in Fig. 1 are similar (viz. they all show a minimum in the region between 0.2 and 0.3 mole fraction alcohol). It can therefore be concluded, from a qualitative viewpoint, that the different functions give similar results. However, from a quantitative viewpoint, there are striking differences. The depth of the minimum, as measured with respect to pure water, ranges from 2 ml/mole for the linear analysis to 26 ml/mole for the Benson-Berson equation (4). Evidently for our interest, namely the effect of solvent composition on ΔV^* , it is necessary to ascertain which analysis is the most reliable. As the measure of reliability we chose to use the ability of the functions to reproduce the experimental data.

After the constants of eqs. [4], [6], and [8] were obtained, the value of $\ln k$ at each of the experimental pressures was calculated, giving $\ln k_{\text{calcd}}$. We then used the deviation, Δ (eq. [10])

$$[10] \quad \Delta = \ln k_{\text{obs}} - \ln k_{\text{calcd}},$$

as a measure of the functional reproducibility (the subscript "obs" refers to the experimental value). For the Benson-Berson equation (eq. [8]) the experimental value of $\ln k_0$ was used in these calculations.

Equation [9] has two unknowns, k_{n+1} and k_n , prohibiting the determination of $\ln k_{\text{calcd}}$. Therefore only the values of $\ln(k_{n+1}/k_n)_{\text{calcd}}$ can be calculated and compared with the observed value. In this case the deviation is given by eq. [11].

$$[11] \quad \Delta = \ln (k_{n+1}/k_n)_{\text{obs}} - \ln (k_{n+1}/k_n)_{\text{calcd}}$$

The Δ values for the four equations are shown in Fig. 2 as a function of pressure for each of the solvents.

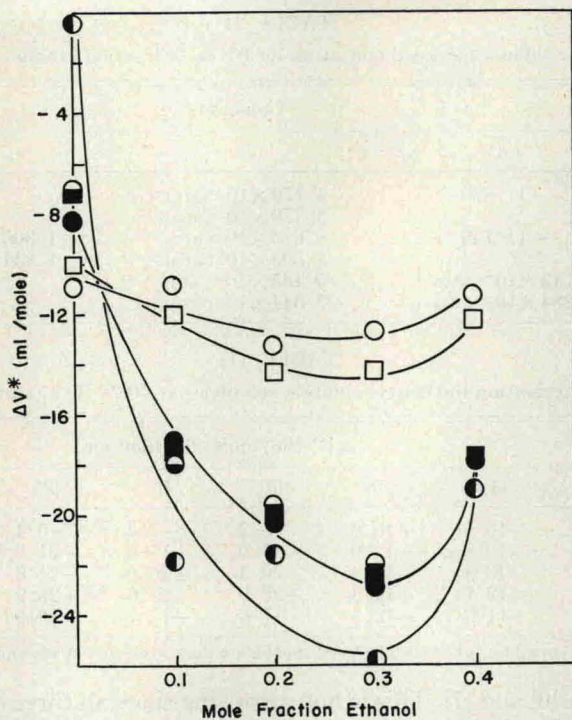


FIG. 1. The variation of ΔV^* with solvent composition: (○) eq. [2]; (□) eq. [3]; (●) eq. [4]; (■) eq. [5]; (◐) eq. [6]; (◑) eq. [7].

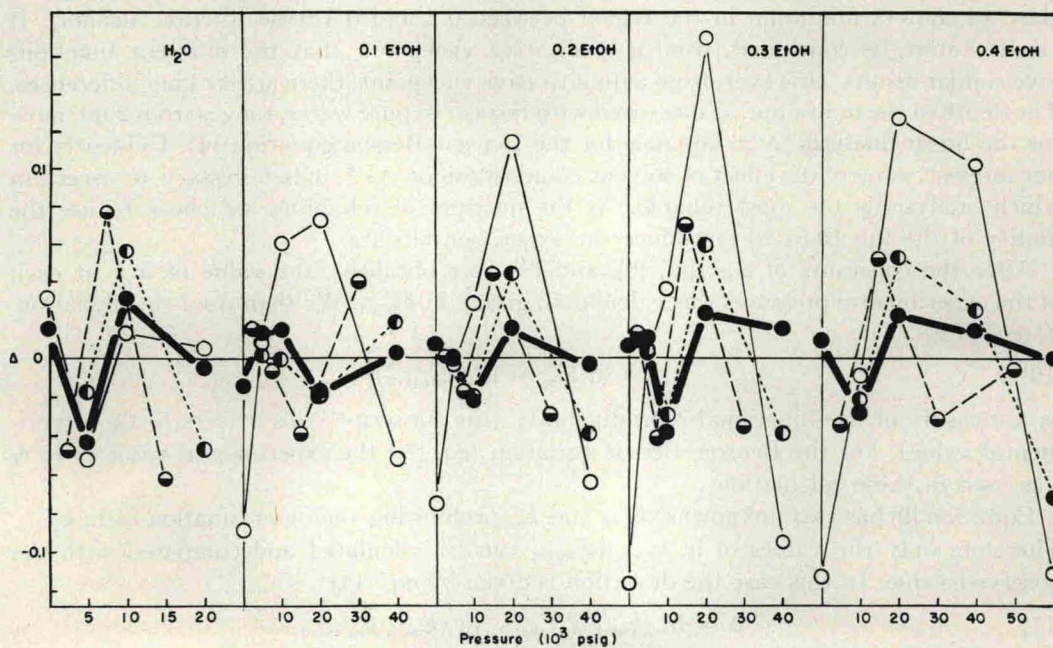


FIG. 2. Variation of the deviation of $\ln k$ with pressure for each solvent: (○) linear analysis (eq. [2]); (●) quadratic analysis (eq. [4]); (◐) Benson-Benson analysis (eq. [6]); (◑) incremental slope analysis (eq. [7]).

The most noticeable feature in Fig. 2 is the systematic error present in the linear analysis (eq. [4]). Only for pure water does the linear relationship appear to give a random error. The fact that systematic errors appear in this function suggests that it is not a reliable representative function of the present data. The second order polynomial, the Benson-Berson equation, and the incremental slope analysis (eqs. [6], [8], and [9]) all appear to give random scatter about zero. The only exception is in the Benson-Berson equation for 0.4 mole fraction ethanol. A further comparison of the four functions is shown in Table IV where the standard deviations are reported.

In accord with the above suggestion, function [4] gives a relatively large standard deviation, whereas eqs. [8] and [9] have values about twice that of eq. [6]. From the data presented in Fig. 2 and Table IV, it is evident that the quadratic function (eq. [6]) best represents our data. It must be emphasized that although we conclude the most reliable function for our data to be a second order polynomial, it need not be generally applicable to all reactions. However, by analogy, we would consider it to be generally applicable to ionic unimolecular decompositions.

TABLE IV
Standard deviation of each function

Function	Number of points	Standard deviation	Relative values
[4]	24	0.0814	4.24
[6]	24	0.0192	1.00
[8]	19	0.0374	1.94
[9]	19	0.0420	2.19

Physical Significance

We have, so far, indicated the empirical merits of various methods of handling kinetic pressure data. An analysis of the physical significance of each would be useful.

The first order polynomial (eq. [4]) ignores the fact that the transition state and substrate may have different isothermal compressibilities. Consequently, the inadequacy of this function in giving a good fit for our data is not unexpected (although Burris and Laidler (8) have found that a linear plot is satisfactory for some S_N2 reactions of ionic species). The use of a second order polynomial recognizes that $(\partial\Delta V^*/\partial p)_T \neq 0$, but requires that $(\partial^2\Delta V^*/\partial p^2)_T = 0$.³

The question arises as to whether our data are precise enough to allow a meaningful calculation of $(\partial\Delta V^*/\partial p)_T$. It is readily seen that (see eqs. [6] and [1])

$$[12] \quad (\partial\Delta V^*/\partial p)_T = -2RTC.$$

For the systems considered in this paper the percent deviation of this derivative (see *Precision Analysis*) lies between 2 and 41%. The actual values of the derivatives and their deviations are presented in Table I.

A good fit of the Benson-Berson equation (eq. [8]) is perhaps not to be expected. Benson and Berson point out that the exact pressure dependence of the rate constant reflects the change in activity coefficient as well as the change in volume during the

³It is true, of course, that $(\partial^2\Delta V^*/\partial p^2)_T$ is not generally zero. The compressibility of a real substance is known to be pressure dependent (13) so that $(\partial^2V/\partial p^2)_T \neq 0$. It would be fortuitous indeed if two states had the same value for this derivative, especially when the polarities of the two differed markedly. Since the polarity of the initial state in the present reaction is practically negligible when compared with that of the transition state, it is not to be expected that the two states have the same value for $(\partial^2V/\partial p^2)_T$. Hence the difference in the values of this derivative cannot be zero, i.e. $(\partial^2\Delta V^*/\partial p^2)_T \neq 0$.

activation process (4). For ionic reactions in water the authors demonstrated that the term due to the activity coefficients is negligibly small, but may become important in solvents of lower dielectric constant. For nonionic reactions, for which this term is zero, these authors used the Tait equation (10) to represent the compressibilities of both the initial and transition states of the reaction (4). This led to the development of eq. [8]. Since this function was developed for nonionic reactions, it appears fortuitous that it gives reasonable results when applied to the analysis of our data for an ionogenic reaction. However, the activity coefficient contribution to $(\partial \ln k/\partial p)_T$ can be shown to be negligible for the systems considered here.

The incremental slope analysis (eq. [9]) was seen to give ΔV_0^* values which coincide with the second order polynomial (Fig. 1). As stated previously, this is because they both allow for the same pressure dependence of ΔV^* . That this is true can be shown by taking the limit of infinitesimal increments and integrating eq. [9] at constant temperature. Thus there is no "a priori" advantage to using one of these methods over the other. However, eq. [6] reproduces the experimental data better than eq. [9] within a factor of two (Table IV). It may be noted that eq. [6] is a strictly analytical function, whereas eq. [9] becomes an analytical function only when the increments become infinitesimal. Therefore, it is not surprising that the two functions do not give identical results. It should also be noted that the incremental slope analysis may suffer from excessive amplification of the effect of the experimental uncertainties in the rate determinations when rate and pressure intervals used become small. Each k and p in the $\ln(k_{n+1}/k_n)$ and $(p_{n+1} - p_n)$ terms has an experimental error associated with it which is independent of the value of the difference between the logarithmic rates and pressures used in each term. Accordingly, as the rate and pressure intervals used become smaller the value of the experimental uncertainties in k and p approach the value of the differences, and increasing scatter of points in the plot of $\ln(k_{n+1}/k_n)/(p_{n+1} - p_n)$ versus $(p_{n+1} + p_n)/2$ is to be expected. This situation is analogous to that which results if one attempts to evaluate enthalpies of activation from two rate determinations at temperatures that are relatively close together. A similar argument was used by Benson and Berson (4) when they neglected the low pressure rates in their study of Walling and Peisach's data for isoprene dimerization (3) because of large scatter. For these reasons, and because eq. [6] is more convenient in that it lends itself to a precision analysis of the type described below, we prefer the quadratic function to the incremental slope analysis.

Precision Analysis

The functional dependence of the rate of benzyl chloride solvolysis on pressure having been established, the next step is to establish the precision of the derivatives. Since we have shown that eq. [6] is the desirable function it is necessary to determine the maximum deviations of the constants. It is convenient to determine these deviations by differentiation (14). By use of the least square functional forms of A , B , and C (eq. [6]), the deviations are given by [13] where f , g , and h are the least square functions for A , B , and C respectively.

$$\begin{aligned}
 dA &= \sum_i \left(\frac{\partial f}{\partial k_i} \right)_{p_j} dk_i + \sum_j \left(\frac{\partial f}{\partial p_j} \right)_{k_i} dp_j \\
 dB &= \sum_i \left(\frac{\partial g}{\partial k_i} \right)_{p_j} dk_i + \sum_j \left(\frac{\partial g}{\partial p_j} \right)_{k_i} dp_j \\
 dC &= \sum_i \left(\frac{\partial h}{\partial k_i} \right)_{p_j} dk_i + \sum_j \left(\frac{\partial h}{\partial p_j} \right)_{k_i} dp_j
 \end{aligned}
 \tag{13}$$

These equations were solved for dA , dB , and dC on an IBM 1620 computer using the average deviation of the rate constants for the dk_i 's and the pressure fluctuation limits for the dp_j 's. The signs of the dp_j and dk_i were taken to be positive in all cases.

The percent deviation in ΔV_0^* is given by $100 dB/B$, whereas that for $(\partial\Delta V^*/\partial p)_T = 100 dC/C$. For the experimental data under consideration in this paper the former has values between 0.9 and 15%, whereas the values for the latter are between 2 and 41%. The actual values for each solvent can be found in Table I.

APPLICATION TO OTHER SYSTEMS

The relative reliability of various functional representations of the data for the pressure dependence of a unimolecular ionogenic reaction having been determined, the applicability of these functions to other reaction types is of interest.⁴

The six reactions studied were (A) bromoacetate with thiosulfate in water (8), (B) methoxide with ethyl bromide in methanol (7), (C) *t*-butyldimethyl sulfonium iodide hydrolysis (15), (D) hydroxide with bromopentammine cobaltic ion in water (8), (E) urea formation in water (16), and (F) isoprene dimerization (3). The ability of each function to reproduce the experimental rate data as a function of pressure for each reaction, together with the values of the activation volumes and the standard deviations, are shown in Fig. 3.

It can be seen that of the six reactions considered, only two (A and C) do not show a systematic error in the linear analysis. Such a situation would be expected for truly linear pressure dependencies. In reaction A all of the analyses give approximately the same value for ΔV^* as well as consistently small values for the standard deviation. In reaction C the Benson-Berson and Whalley analyses give systematic errors.

Reactions B, D, and E are much better represented by the quadratic than the linear analysis (Fig. 3). Since B was designed to demonstrate a viscosity inhibition of a bimolecular reaction in solution (7), it is not surprising that the pressure dependence is nonlinear. The fact that the Benson-Berson and Whalley treatments give rather large standard deviations is somewhat surprising, as is the fact that the Benson-Berson analysis gives a standard deviation only half as large as the quadratic analysis for reaction D. It would seem that this analysis is suited to a wider variety of systems than suggested by the original authors (4). Reaction E has identical values of the standard deviation for the quadratic and Benson-Berson analyses, but a large difference in the ΔV^* values from the two methods. Unfortunately there is no way of distinguishing between their reliability.

A great deal of attention has been given to the pressure dependence of reaction F as evidence by the papers of Walling and Peisach (3), Benson and Berson (4), and rebuttals by both groups of workers (9, 17). Benson and Berson disregarded the low pressure rate constants in analyzing the data for this reaction because of much scatter of the points (*vide supra*) (4), and obtained an activation volume some 50% more negative than the original authors (3). In this study, all of the rate constants were used, and it can be seen that, except for the linear analysis, the activation volumes are all very similar (Fig. 3F). A glance at Fig. 3F indicates that if any of the points were to be omitted, those between 3 500 and 5 500 kg/cm² should be the likely candidates. The value of -30.4 ml/mole obtained from the quadratic analysis lies midway between those calculated by the two sets of authors (-24.3 (3) and -36.5 (4) ml/mole).

⁴This suggestion was originally made by E. M. Arnett to J. B. Hyne.

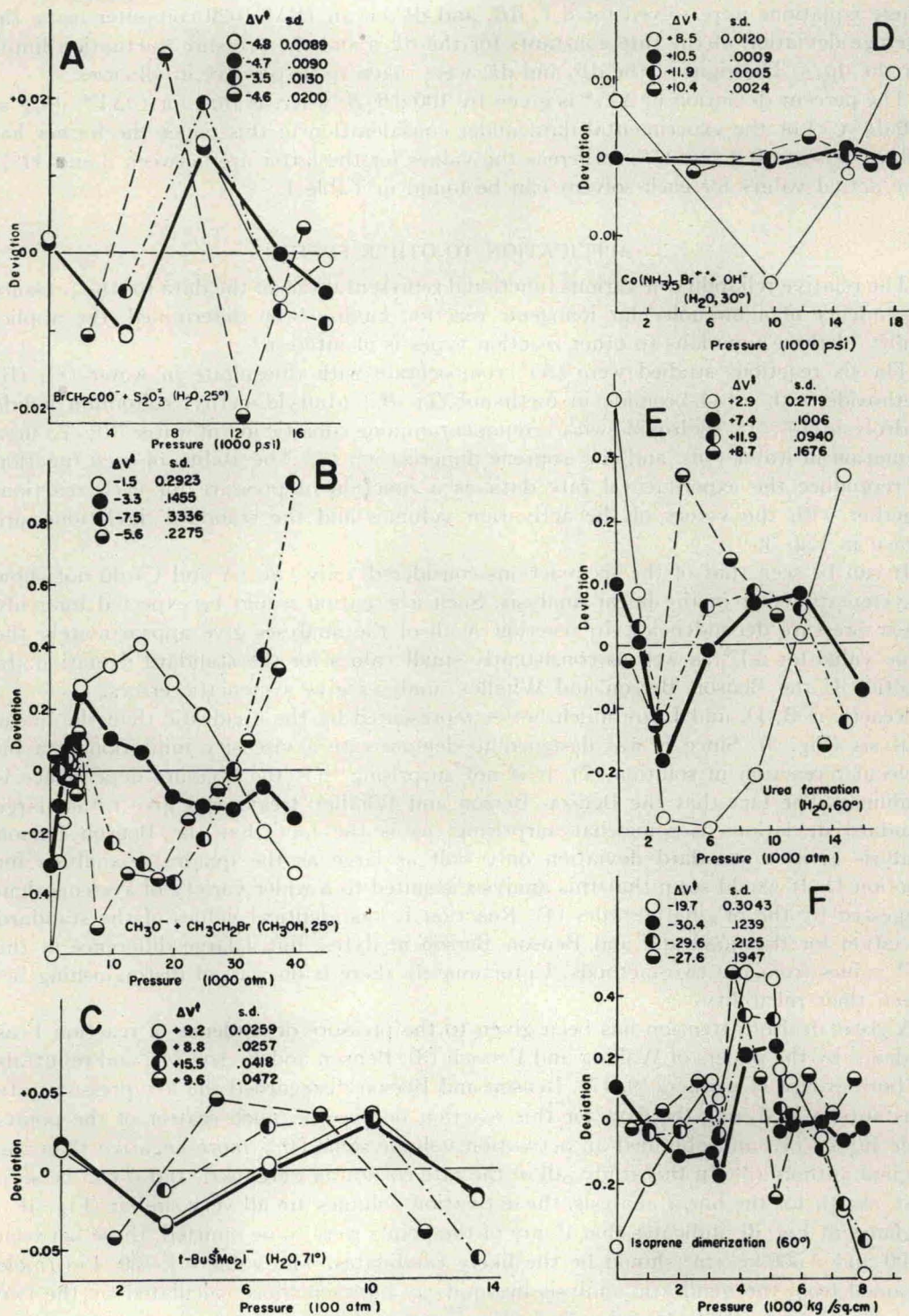


FIG. 3. Variation of the deviation of $\ln k$ with pressure for six reactions. (○) linear function; (●) quadratic function; (◐) Benson-Berson function; (◑) incremental function.

CONCLUSION

In summary it can be concluded that: (1) A quadratic polynomial is generally the best representation of the pressure dependence of a logarithmic rate constant regardless of the reaction type; (2) it appears *necessary* and *sufficient* to allow for the non-zero pressure dependence of activation volumes, and *this dependence is measurable*; and (3) differentiation of the appropriate function gives rise to a precise measurement of activation parameters.

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