

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.

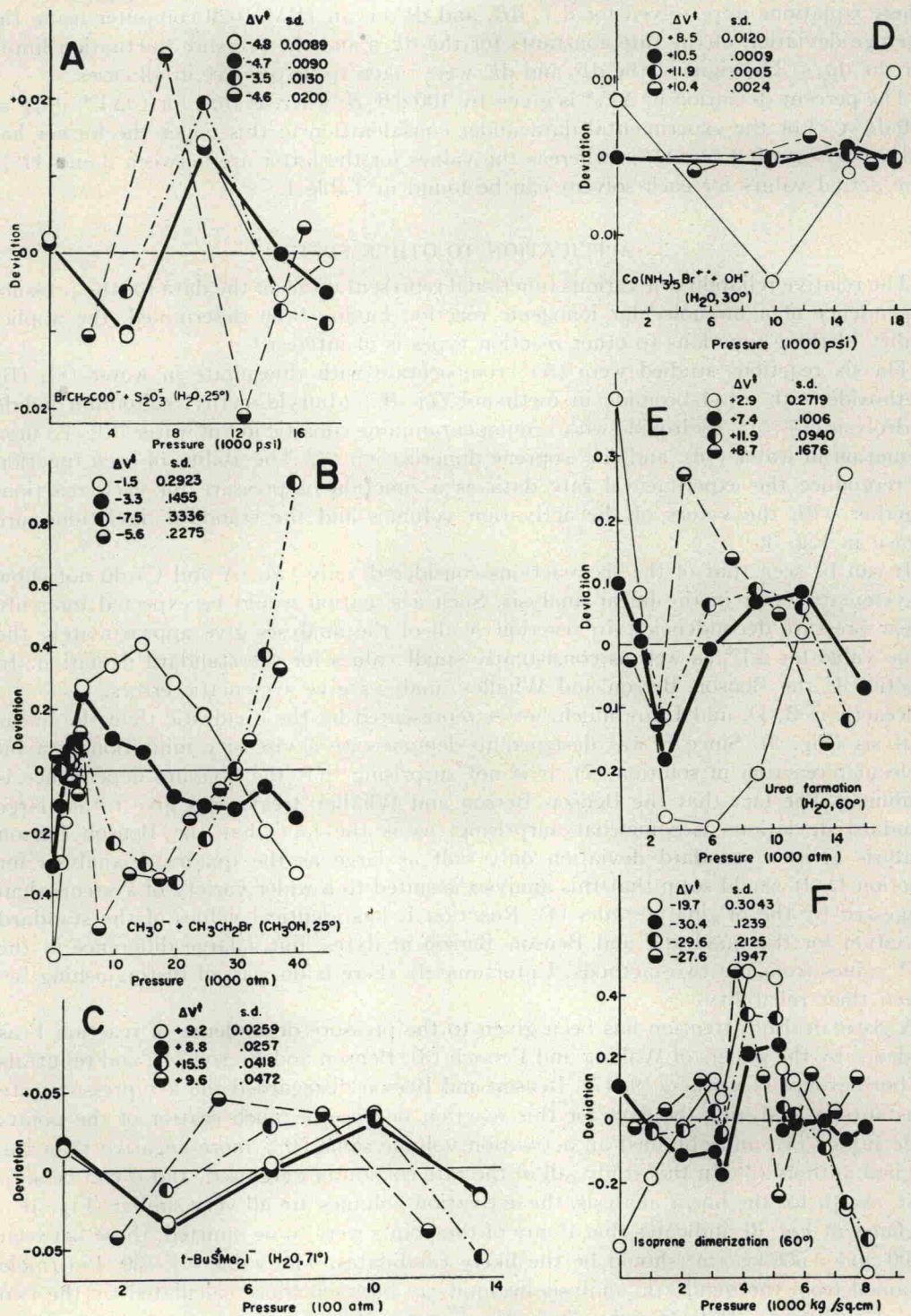


FIG. 3. Variation of the deviation of $\ln k$ with pressure for six reactions. (○) linear function; (●) quadratic function; (◐) Benson-Berson function; (◑) incremental function.