

THE EFFECT OF PRESSURE IN SOME REACTIONS CHARACTERIZED BY Ar_1^- - PARTICIPATION¹

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In two earlier publications² we discussed activation volumes of a number of solvolysis reactions considered by many chemists to proceed at enhanced rates because of neighboring group participation. This activation parameter, the value of which is typically³ of the order of -15 - -20 $cm^3/mole$ for solvolysis, was observed to be somewhat less negative in cases characterized by σ -participation, and somewhat more negative in cases involving π -participation. Although these effects are in agreement with both empirical and theoretical expectations, they are small, not capable of very precise measurement, and subject to such coincidental features as the efficiency of packing of solvent molecules about both initial and transition states, and it seemed therefore incumbent on us to demonstrate the soundness of our basic premise by means of some examples in which neither the intervention of participation nor the estimated magnitude of its effect on the volume of activation could be subject to any reasonable doubt. The base-promoted solvolyses of 4-p-hydroxyphenyl-1-butyl brosylate and of 2-p-hydroxyphenylethyl chloride provide us with such examples.

The brosylate undergoes tert-butanolysis at least fifty times faster in tert-butanol containing a small excess of base than in the neutral alcohol and it gives spiro(4,5)deca-1,4-dien-3-one as the principal product,⁴ so that Ar_1^- - 5 participation is clearly occurring. The pressure effect predicted in such a reaction is unique in that it should resemble values typical of S_N2 displacements (-5 - -10 $cm^3/mole$) rather than those of solvolysis.³ The argument is that no new charges are formed in the reaction; a charge already there is merely transferred to another atom with the concomitant

bond making and breaking processes characteristic of such displacement reactions. The nosylate was prepared by the general route described by Baird and Winstein⁴; m.p. 57.5-59° (lit.⁴ 59.3-61.7°). 1-Propanol was used rather than tert-butanol because the high freezing point of the latter (25.5°) precludes its use as a solvent in high pressure studies. The reaction was carried out at 25° in the presence of 20% excess potassium 1-propoxide, and followed during the first half of the reaction by titration with standard base after quenching with a small excess of standard p-toluenesulfonic acid in methanol. The high pressure apparatus and general techniques were used without modification as previously described.⁵ Good first-order plots were obtained; a check of our procedures with tert-butanol yielded $k_1 = 3.71 \times 10^{-5} \text{ sec}^{-1}$, as compared with a reported value⁴ of $4.16 \times 10^{-5} \text{ sec}^{-1}$. In 1-propanol, k was found to be $3.11 \times 10^{-5} \text{ sec}^{-1}$. The high pressure measurements, extended over a range of about 4 kbar, yielded an activation volume of $-5.4 \pm 1.0 \text{ cm}^3/\text{mole}$ (see Fig. 1).

For our reference solvolysis, we used 4-p-anisyl-1-butyl nosylate; m.p. 55.5-56°; nmr spectrum: τ (CDCl₃) 1.82 (4H, q), 3.13 (4H, q), 5.90 (2H, t), 6.28 (3H, s), 7.48 (2H, m), 8.32 (4H, m); anal: calcd. for C₁₇H₁₉NO₆S: C, 55.88; H, 5.24; N, 3.83; S, 8.78; found: C, 55.73; H, 5.17; N, 3.75; S, 8.95. Its solvolysis rate was studied in 1-propanol containing 2% water (by volume) at 40° by means of a high pressure conductance cell recently built in this laboratory⁶; these changes in leaving group, medium, temperature and analytical technique were all related to the fact that the change of the phenoxy anionic group by a neutral anisyl group causes a considerable rate depression. It was established independently⁶ that none of these changes affect ΔV_0^\ddagger by more than 1 cm³/mole in other solvolysis reactions. At one atmosphere the rate constant, again measured during the first half of the reaction, was found to be $7.97 \times 10^{-6} \text{ sec}^{-1}$; the activation volume is $-21.0 \pm 1.0 \text{ cm}^3/\text{mole}$. It is clear⁷ that the observed rate of 1-propanolysis of the nosylate is the sum of anchimerically assisted and unassisted components; however, the difference in activation volume between these two paths is likely to be small, and we need therefore not be concerned with the extent to which participation by the neutral anisyl group is occurring in this case.

2-p-Hydroxyphenylethyl chloride, m.p. 56.8-57.5° (lit.⁸ 55.3-57°) was solvolyzed in 1-propanol containing a two-fold excess of potassium 1-propoxide at 16°. The reaction

was followed by means of standard chloride titrations after quenching with dilute nitric acid; a mercury-mercuric sulfate reference electrode was used. At atmospheric pressure the rate constant was found to be $1.11 \times 10^{-5} \text{ sec}^{-1}$; the activation volume was $-1 \pm 1 \text{ cm}^3/\text{mole}$. This value is somewhat higher than that of the butyl analog, but these two numbers are not directly comparable. On the one hand, chlorides are expected to lead to a more negative activation volume than benzene-

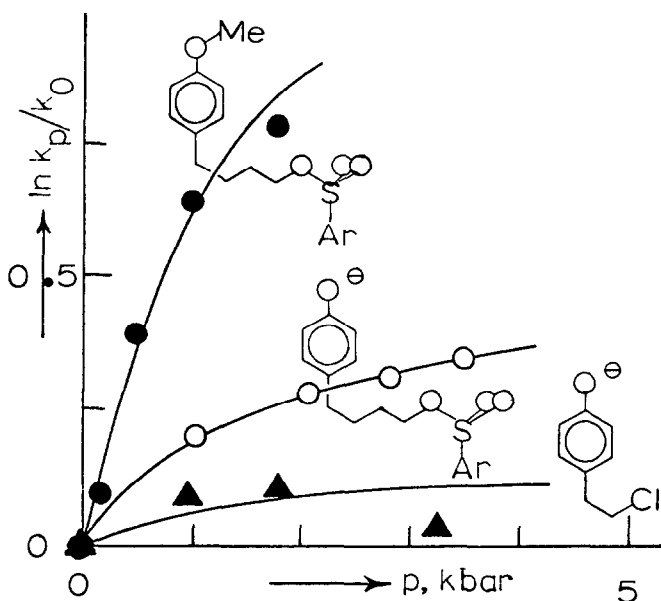


Figure 1. The effect of pressure on the rates of several 1-propanolysis reactions.

sulfonate esters because of charge dispersal in the latter, but this is at least compensated by the large parachor correction ($+12.5 \text{ cm}^3/\text{mole}$)⁹ of the incipient cyclopropyl ring system of the initial product, spiro(2,5)octa-1,4-dien-3-one. The enormous rate acceleration of this reaction compared to that of the solvolysis of the corresponding anisyl compound ($\sim 10^6$) makes it impossible to make a direct comparison of the activation volumes in this case. The conclusion is nevertheless clear: since solvolyses are normally characterized by activation volumes of -15 - $-20 \text{ cm}^3/\text{mole}$, the fact that a value of 0 - $-5 \text{ cm}^3/\text{mole}$ is observed in two cases clearly involving Ar_1^- participation demonstrates the predictability of high pressure rate effects in such reactions.

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