

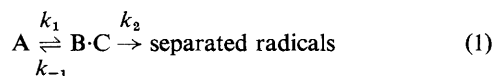
Chemical Kinetics at very High Pressures. A Pressure-induced Cage Effect in an Ion-producing Reaction

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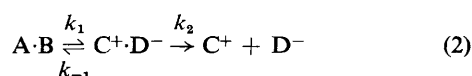
The solvolysis of isopropyl bromide in a methanol–ethanol mixture becomes controlled by the diffusion apart of the product ions at pressures greater than 40 kbar; diffusion control of similar reactions at high pressures should therefore be very common.

The rates of many free-radical decompositions, either thermal or photochemical, are controlled by the diffusion apart of the products, *i.e.* by the so-called cage effect. The process can be schematically represented by reaction (1) where B and C are



free radicals generated from A either thermally or photochemically, and the dot shows that they are in contact. If k_2 is much smaller than the rate constant k_{-1} for recombination or the rate constant for the production of other stable products, the reaction is diffusion-controlled.¹

There is nothing in principle that confines such effects to free-radical decompositions but, although diffusion control in ionic reactions is frequently mentioned, there are few specific examples. One of these occurs in the hydrolysis of *N*-substituted maleamic acids, for some of which the diffusion apart of the product anhydride and amine appears to be rate controlling.²



They should, however, be very common. For example, the solvolysis (2) where A and B represent a solvent and a reactant molecule respectively, C^+ and D^- represent ions resulting from their reaction, and the centred plus sign indicates molecules randomly distributed, is rarely diffusion-controlled for common simple ion-producing reactions in ordinary solvents. The volume of activation of a typical solvolysis of an alkyl halide in a solvent like methanol or ethanol, *i.e.* of step 1 of solvolysis (2), is *ca.* $-30 \text{ cm}^3 \text{ mol}^{-1}$ at zero pressure^{3,4} and increases to *ca.* $-3 \text{ cm}^3 \text{ mol}^{-1}$ at 40 kbar.⁵ The volume of activation of the reverse step is not known, but is probably a fraction of the value for the forward step and positive. The volume of activation of step 2 is the volume of activation of the diffusion coefficient or, approximately, the volume of activation of the viscosity. The volume of activation of the viscosity, which is defined as $RT \partial \ln \eta / \partial p$, where R is the gas constant, T the temperature, η the viscosity, and p the pressure is *ca.* $5 \text{ cm}^3 \text{ mol}^{-1}$ in, say, methanol at zero pressure as calculated from the published data.⁶ At low pressure, increasing the pressure may cause little change in k_{-1}/k_2 . At high pressure, however, the viscosity–pressure curve is sigmoidal in shape^{7,8} and the volume of activation increases greatly with increasing pressure and formally becomes effectively infinite at the glass transition.

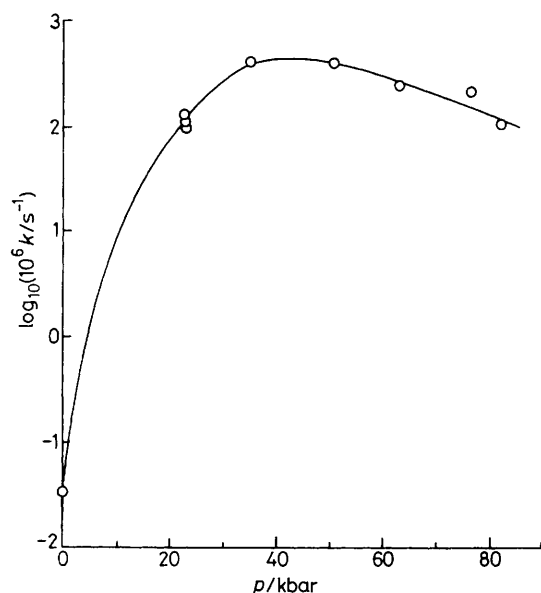


Figure 1. Graph of the rate constant of the solvolysis of isopropyl bromide in MeOH-EtOH in the range 0–80 kbar at 46 °C. The value at zero pressure was assumed to be that of the solvolysis of 2-butyl bromide in ethanol extrapolated from the range 130–170 °C (ref. 13). The curve was drawn so that the slope at zero pressure is $-30 \text{ cm}^3 \text{ mol}^{-1}$ (ref. 3, 4).

High pressures will, therefore, greatly increase the ratio k_{-1}/k_2 and should eventually cause the diffusion step 2 to be rate-limiting for all solvolyses in solvents that become glassy instead of freezing. The purpose of the work reported in this paper was to find a solvolysis that becomes diffusion controlled under pressure.

The reaction studied is the solvolysis of isopropyl bromide in a 4:1 v/v methanol-ethanol mixture at 46 °C. The sample was held between two tungsten carbide anvils, having 12 mm faces, using a gasket of glass-impregnated epoxy resin or other non-conductor.^{9,10} The reaction was followed by its electrical conductance using the anvils as electrodes. The anvils were pushed together by a 250 ton hydraulic press, and the pressure was calibrated by the transitions liquid-to-ice-VI¹¹ and ice-VI-to-ice-VII.¹²

The rate constant is plotted against the pressure in Figure 1. The value at zero pressure was assumed to be that for *s*-butyl bromide in ethanol, as obtained by extrapolating published data,¹³ and the curve at low pressures was drawn assuming that the volume of activation at zero pressure is $-30 \text{ cm}^3 \text{ mol}^{-1}$.^{3,4} The rate constant passes through a maximum at ca. 40 kbar, and the volume of activation at 70 kbar is $0.9 \text{ cm}^3 \text{ mol}^{-1}$.

The solvolysis, in which the reactants and transition state are $\text{MeOH} \cdot \text{RBr}$ and $\text{MeOH}^{\delta+} \cdot \text{R} \cdot \text{Br}^{\delta-}$, respectively, or the corresponding ethyl compounds, is unlikely to have a positive volume of activation at any pressure because of the contraction caused by the high dipole moment of the transition state. The reaction is, therefore, very probably controlled by the diffusion apart of the products.

If $k_{-1}/k_2 \ll 1$ at 70 kbar, the measured rate constant is $K_1 k_2$ where K_1 is the equilibrium constant for the production of the ion pair. If k_2 is inversely proportional to the viscosity, the volume of activation ΔV_2^\ddagger of step 2 is $5 \text{ cm}^3 \text{ mol}^{-1}$ from the data of Piermarini *et al.*⁸ adjusted to 46 °C using Bridgman's⁶ measurements up to 12 kbar, and so the volume change of step 1 at 70 kbar and 46 °C is ca. $-4 \text{ cm}^3 \text{ mol}^{-1}$.

By assuming that the equilibrium constant for step 2 is described by Fuoss's theory¹⁴ and the rate constant k_{-2} for the diffusion of the ions together is described by the Smoluchowski-Debye equation,¹⁵ k_2 was estimated to be ca. 10^4 s^{-1} at 70 kbar. From this value and the interpolated rate constant, the equilibrium constant K_1 for the production of the ion pair is ca. 2×10^{-8} at 70 kbar and 46 °C, and the change of Gibbs function is 47 kJ mol^{-1} .

It seems, then, that chemical kinetics at very high pressure can provide new kinds of information about organic reactions. Very high pressure may also be useful for synthesis, *e.g.* if the ion pair $\text{C}^+ \cdot \text{D}^-$ in solvolysis (2) can recombine to form a more stable product than $\text{A} \cdot \text{B}$ that may be difficult to make.

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