

Effect of Pressure on the Rate of Hydrolysis of Methyl and Isopropyl Bromides

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The rate constants for the spontaneous hydrolysis of methyl and isopropyl bromides in water have been measured to an accuracy of about 0.2% up to 3 kbars at three temperatures. The shape of the rate-constant-pressure curve for methyl bromide shows clearly that a second mechanism occurs at high pressures. The high-pressure mechanism has perhaps more covalent attachment of water in the transition state, *i.e.*, is more $\text{S}_{\text{N}}2$ -like, than the low-pressure mechanism. The results for isopropyl bromide are consistent with, but do not prove, a similar but more reluctant change of mechanism with pressure. The activation volume for both reactions becomes less negative with increasing temperature at 1 bar, but this trend reverses at about 500 bars. The activation enthalpy and entropy vary with pressure in a complicated fashion, partly although not entirely connected with the change of mechanism. The constant-volume heat capacity of activation is about $-93 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for both reactions, which is about twice the constant-pressure heat capacity. It varies much less with pressure but much more with temperature than the constant-pressure heat capacity. A detailed interpretation of this unexpected behavior is premature at present.

1. Introduction

The temperature dependence of the constant-pressure activation enthalpy $\Delta H_p^\ddagger$ is usually described by an activation heat capacity at constant pressure $\Delta C_p^\ddagger$ defined by

$$\Delta C_p^\ddagger = (\partial \Delta H_p^\ddagger / \partial T)_p \quad (1)$$

In recent years many measurements of this quantity have been made¹ with a view to correlating it with mechanism. All these attempts, however, suffer from a disadvantage common to all attempts to interpret heat capacities of condensed phases at constant pressure, namely that part of the energy required to increase the temperature goes to expanding the system against its own internal forces. Unless the magnitude of this energy can be estimated, it is not possible to discuss the various contributions to the heat capacity of activation with any accuracy. The heat capacity of activation at constant volume $\Delta C_v^\ddagger$

$$\Delta C_v^\ddagger = (\partial \Delta U_v^\ddagger / \partial T)_v \quad (2)$$

where $\Delta U_v^\ddagger$ is the internal energy of activation at constant volume, ought to be more informative than $\Delta C_p^\ddagger$, but no previous attempt to measure it has been reported. The relationship between the two heat capacities of activation is²

$$\Delta C_p^\ddagger - \Delta C_v^\ddagger = \frac{T\alpha\Delta V^\ddagger}{\kappa} \left\{ \left(\frac{\partial}{\partial T} \ln \frac{\alpha\Delta V^\ddagger}{\kappa^2} \right)_p + \frac{\alpha}{\kappa} \left(\frac{\partial}{\partial p} \ln \frac{\Delta V^\ddagger}{\kappa} \right)_T \right\} \quad (3)$$

where T is the temperature, p is the pressure, α and κ are the thermal expansivity and compressibility of the mixture, and $\Delta V^\ddagger$ is the activation volume. An estimate of the magnitude of the difference between the

two heat capacities for the neutral hydrolysis of ethylene oxide in water³ gave⁴ roughly $-30 \text{ cal deg}^{-1} \text{ mol}^{-1}$. This is of the magnitude of $\Delta C_p^\ddagger$ for many reactions, and it shows that the two heat capacities can differ significantly.

This paper describes the measurement of the quantities required to determine $\Delta C_p^\ddagger - \Delta C_v^\ddagger$ for the hydrolysis of methyl and isopropyl bromides in water. These reactions were chosen because there is already a large amount of accurate information about them,⁵⁻⁸ including several measurements of the heat capacity of activation at constant pressure, and they typify an important class of solvolyses. Furthermore, to measure $\Delta C_p^\ddagger - \Delta C_v^\ddagger$ by means of eq 3, the activation volume and its temperature and pressure coefficients are required. To determine these coefficients, accurate rate constants are required and these reactions can conveniently and accurately be followed by conductance measurements.

Unfortunately, for a present understanding of these reactions the measurements have revealed unexpected complexities, and emphasize our ignorance more than our understanding. The most significant information is probably a sigmoid variation of $\ln k$ in the pressure for methyl bromide, which is interpreted as due to a change of mechanism.

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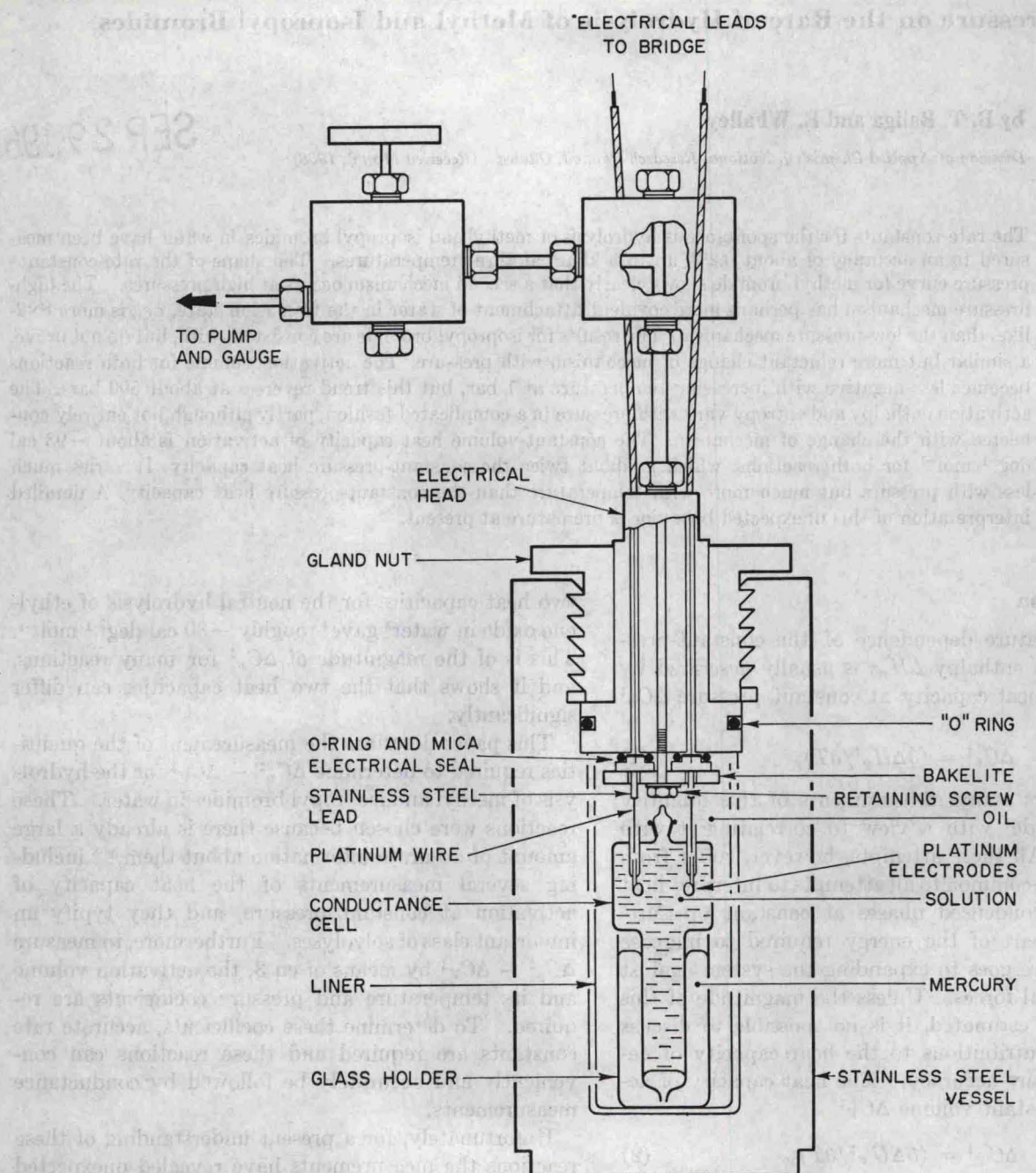


Figure 1. Sketch of conductance cell and pressure vessel.

2. Experimental Methods

Materials. Methyl bromide from a Matheson of Canada lecture bottle analyzed 99.9% by gas chromatography, and was used directly. Eastman Kodak White Label isopropyl bromide was refluxed over anhydrous sodium sulfate and distilled, and the middle fraction boiling at 59.5–60.0° was collected. It analyzed 99.7% by gas chromatography. Distilled water was freed of carbon dioxide by boiling and was stored out of contact with carbon dioxide. The conductance in the cell used was $<0.8 \mu\text{mho}$.

Pressure Techniques. The pressure equipment is shown in Figure 1. The pressure vessel is of the kind

used previously,⁹ with the head modified for electrical seals. The electrical seals were made with mica and Viton O-rings as described elsewhere¹⁰ and were held in place by a Bakelite retaining plate. The resistance between leads and between a lead and the head was >100 megohms at all pressures and temperatures.

The pressure-transmitting fluid was medium grade Stanolax, and pressure was generated by an air-driven oil pump and adjusted by a screw injector. The rate constants obtained in this work are reproducible to 0.1

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