

due to pressure. The ratio of these rates to the rates found by the direct method (which are independent of the fate of the free radicals after dissociation) are shown in table 1 and are an indication of the efficiency of AZBN as a source of available free radicals.

A much more stringent test of the assumption that the effect of pressure on free-radical dissociations is solely due to the volume changes involved in breaking a bond, should be provided by the measurements of the dissociation constant of nitrogen tetroxide. Not only should the result of the calculation here be independent of any assumptions regarding the activated state, but there are also much more accurate data available on which to base a theoretical calculation of the volume change.

By using X-ray diffraction data on N_2O_4 ¹⁷ and electron diffraction data on NO_2 ¹⁸ for the bond lengths and van der Waals radii for the atoms one finds that there is a volume increase of 2.1 cm^3 when one mole of nitrogen tetroxide dissociates. From the data of table 2 one can on the other hand derive that the pressure effect on the dissociation constant is equivalent to a volume increase of about $23 \text{ cm}^3/\text{mole}$. In this case therefore the assumptions made about the effect of pressure on the dissociation are quite inadequate. It is concluded that there is some interaction between the solvent and the nitrogen oxides which is changed by the application of pressure.

The retardation of free-radical dissociations by pressure found in these experiments is of the kind one would expect from general considerations but which so far has never been demonstrated experimentally. Merrett and Norrish¹⁹ refer to some measurements of the rate of dissociation of benzoyl peroxide under pressure, but these appear never to have been published.

It follows from the present results that the large acceleration of polymerization reactions by pressure, which has been observed,¹⁹ is not due to an increase in the rate of initiation but must be due to some other step in the polymerization.

It is a pleasure to acknowledge the help and stimulus derived from many discussions with Dr. S. D. Hamann and the help of Mr. H. G. David in running the high-pressure equipment.

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due to pressure. The ratio of these rates to the rates found by the direct method which are independent of the rate of the free radicals after dissociation are shown in Table I and are an indication of the efficiency of AXB₂ as a source of available free radicals.

A most interesting test of the assumption that the effect of pressure on free radical dissociation is solely due to the volume changes involved in breaking a bond should be provided by the measurement of the dissociation constant of various esters. Not only should the result of the calculation have to be independent of any assumptions regarding the activated state, but there is also much more accurate data available on which to base a theoretical calculation of the volume change.

(b) Using X-ray diffraction data on N₂O₄ and electron diffraction data on NO₂ for the bond lengths and van der Waals radii for the atoms one finds that there is a volume increase of 2.1 cm³ when one mole of nitrogen tetroxide dissociates. From the data in Table I one can see on the other hand that the pressure effect on the dissociation constant is equivalent to a volume increase of about 23 cm³ mole. In this case therefore the assumptions made about the effect of pressure on the dissociation are quite inadequate. It is concluded that there is some interaction between the solvent and the nitrogen oxides which is changed by the application of pressure.

The retardation of free radical dissociation by hydrogen found in these experiments is of the kind one would expect from considerations of the kind so far has been discussed by H. G. Hamann and M. G. K. David in connection with the reaction of benzoyl peroxide under pressure, but these experiments have never been published.

It follows from this present result that the large acceleration of polymerization rate of initiation but must be due to some other step in the polymerization.

It is a pleasure to acknowledge the help and stimulus derived from many discussions with Dr K. D. Hamann and the help of Mr H. G. David in running the high-pressure equipment.

The work described in this paper was carried out as part of the research programme of the Division of Industrial Chemistry of the Commonwealth Scientific and Industrial Research Organization, Australia.

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