

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  $N_2O_4$ <sup>17</sup> and electron diffraction data on  $NO_2$ <sup>18</sup> for the bond lengths and van der Waals radii for the atoms one finds that there is a volume increase of 2.1 cm<sup>3</sup> 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 cm<sup>3</sup>/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 Norrish<sup>19</sup> 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,<sup>19</sup> is not due to an increase in the rate of initiation but must be due to some other step in the polymerization.

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<sup>1</sup> Buchanan and Hamann, *Trans. Faraday Soc.*, 1953, **49**, 1425.

<sup>2</sup> David and Hamann, *Trans. Faraday Soc.*, 1954, **50**, 1188.

<sup>3</sup> Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51**, 1684.

<sup>4</sup> Burris and Laidler, *Trans. Faraday Soc.*, 1955, **51**, 1497.

<sup>5</sup> Talât-Erben and Bywater, *J. Amer. Chem. Soc.*, 1955, **77**, 3710, 3712.

<sup>6</sup> Hammond, Sen and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

<sup>7</sup> Roy, Nash, Williams and Hamill, *J. Amer. Chem. Soc.*, 1956, **78**, 519.

<sup>8</sup> Ziegler, Ewald and Orth, *Annalen*, 1930, **479**, 277.

<sup>9</sup> Bachmann and Osborn, *J. Org. Chem.*, 1940, **5**, 29.

<sup>10</sup> Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.

<sup>11</sup> Ewald and Hamann, *Austral. J. Chem.*, 1956, **9**, 54.

<sup>12</sup> Thiele and Heuser, *Annalen*, 1896, **290**, 1.

<sup>13</sup> Bachmann and Wiselogle, *J. Org. Chem.*, 1936, **1**, 354.

<sup>14</sup> Attwood and Roleffson, *J. Chem. Physics*, 1941, **9**, 506.

<sup>15</sup> Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1930, **66**, 213.

<sup>16</sup> Glasstone, Laidler and Eyring, *Theory of Rate Processes* (McGraw-Hill, New York, 1941), p. 470.

<sup>17</sup> Broadley and Robertson, *Nature*, 1949, **164**, 915.

<sup>18</sup> Maxwell and Mosley, *J. Chem. Physics*, 1940, **8**, 738.

<sup>19</sup> Merrett and Norrish, *Proc. Roy. Soc. A*, 1951, **206**, 309.

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

A much more stringent test of the assumption that the effect of pressure on local radical desorption is solely due to the volume changes involved in packing a bond should be provided by the measurements of the desorption constant of various monomers. Not only should the result of the calculation here be independent of any assumptions regarding the activated state, but there should be much more accurate data available on which to base a theoretical calculation of the volume change.

By using X-ray diffraction data on  $MgO$ ,  $CaO$  and sodium chloride data on  $KCl$  for the bond lengths and van der Waals radii for the atoms one finds that there is a volume increase of 2.1 only when one mole of nitrogen molecules desorbs. From the data in Table I one can see on the other hand that the pressure effect on the desorption constant is equivalent to a volume increase of about 23 cm<sup>3</sup>/mole. In this case therefore the assumptions made about the effect of pressure on the desorption 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 extraction of free-radical desorption by pressure found in this experiment is of the kind one might expect from the considerations here which so far has never been reported. The University Press, Aberdeen, Scotland, has been asked to publish this paper but these authors never to have been published.

It follows from this report that the large acceleration of polymerization rate of initiation 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. Hamman and the help of Mr H. G. David in carrying out the high-pressure equipment.

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

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