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The rates of dissociation of 2,2'-azobis(isobutyronitrile) (AIBN) and benzoin  
oxide (BO) have been measured in toluene at pressures up to 10,000 and 1500 atm  
respectively and were found to be increased by hydrostatic pressure. The effect is  
markedly more consistent with the volume change due to a 10% dissociation of the reacting  
species in toluene than with the volume change due to a 10% dissociation with AIBN  
in benzoin oxide. The effect is more consistent with the volume change due to a 10%  
dissociation of the reacting species in benzoin oxide than with the volume change  
due to a 10% dissociation of the reacting species in toluene.

**LIQUID-PHASE FREE-RADICAL DISSOCIATIONS AT  
HIGH PRESSURE**

The effect of pressure on the rates of ionic reactions can largely be explained  
in terms of the changes in the energy of activation brought about by pressure.  
The rates of free-radical dissociations are known to be little influenced by the  
nature of the reaction medium and it is therefore unlikely that solution energies  
are major factors in the energy changes of such reactions. One would thus expect  
the effect of pressure on these reactions to be much smaller than for ionic reactions.

In the present investigation the effect of pressure on three free-radical dis-  
sociations has been observed. The rate of dissociation of 2,2'-azobis(isobutyro-  
nitrile) (AIBN) in toluene has been measured in two ways; the disappearance of  
AIBN was followed directly by observing the light absorption at three character-  
istic wavelengths, and the formation of free radicals was observed indirectly  
by using iodine as a scavenger and following its disappearance on a photo-  
meter. By the direct method measurements were made at 1 and 1500 atm  
at 70°C while the scavenger method was used to follow the reaction up to 10,000  
atm at 67°C.

The use of iodine in measuring the dissociation of AIBN has been investigated  
in some detail by Hatanaka et al.<sup>1</sup> who found the efficiency of the scavenging  
reaction to vary in different solvents. It is known that the "cage effect" is very  
prominent in this dissociation due to the possibility that the two primary free-  
radical fragments react to form nitrogen dioxide and form the stable tetramethyl-  
succinonitrile before they diffuse apart (Challa et al.).<sup>2</sup>

This effect is specific to AIBN and should not apply to the dissociation of  
peroxyacetone (PTE) which was investigated as the second substance. The  
use of iodine to measure the rate of this type of dissociation was first introduced  
by Ziegler, Ewald and O'Leary<sup>3</sup> and was widely used by Hatanaka.<sup>1</sup> Since the  
formation of triphenylmethyl iodide in this reaction with iodine is reversible these  
workers found it necessary to introduce pyridine and ethanol to react further with  
the iodide. In the present investigation the need for this was avoided by using  
a large excess of PTE and following only the first few percent of the dissociation  
in the region of Hawn and Mellett.<sup>4</sup> The dissociation of PTE was measured  
in toluene at 50°C and at pressures up to 1500 atm.

The third system investigated was the equilibrium between nitrogen tetroxide  
and nitrogen dioxide in carbon tetrachloride solution. This equilibrium was  
measured at 25 and 31°C and at pressures up to 1500 atm.

## LIQUID-PHASE FREE-RADICAL DISSOCIATIONS AT HIGH PRESSURE

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The rates of dissociation of 2:2'-azo-bis-isobutyronitrile (AZBN) and pentaphenylethane (PPE) have been measured in toluene at pressures up to 10,000 and 1500 atm respectively and were found to be decreased by hydrostatic pressure. The effect is as predicted by considering only the volume change due to a 10 % extension of the reacting bond in forming the activated state, although when using iodine as a scavenger with AZBN one finds a much larger pressure effect, presumably due to changes in the "cage effect". The pressure effect on the dissociation equilibrium of nitrogen tetroxide in carbon tetrachloride solution has been measured at pressures up to 1500 atm and was found to be ten times as great as predicted from the changes in molecular volumes.

The effect of pressure on the rates of ionic reactions can largely be explained in terms of the changes in the energy of solvation brought about by pressure.<sup>1, 2, 3, 4</sup> The rates of free-radical dissociations are known to be little influenced by the nature of the reaction medium and it is therefore unlikely that solvation energies are major factors in the energy changes of such reactions. One would thus expect the effect of pressure on these reactions to be much smaller than for ionic reactions.

In the present investigation the effect of pressure on three free-radical dissociations has been observed. The rate of dissociation of 2:2'-azo-bis-isobutyronitrile (AZBN) in toluene has been measured in two ways; the disappearance of AZBN was followed directly by observing the light absorption at three characteristic wavelengths,<sup>5</sup> and the formation of free radicals was observed indirectly by using iodine as a scavenger and following its disappearance on a spectrophotometer.<sup>6</sup> By the direct method, measurements were made at 1 and 1500 atm at 70° C, while the scavenger method was used to follow the reaction up to 10,000 atm at 62.5° C.

The use of iodine in measuring the dissociation of AZBN has been investigated in some detail by Hammond *et al.*<sup>6</sup> who found the efficiency of the scavenging reaction to vary in different solvents. It is known that the "cage effect" is very pronounced in this dissociation due to the possibility that the two primary free-radical fragments react to eliminate nitrogen and form the stable tetramethylsuccinodinitrile before they diffuse apart (Hamill *et al.*).<sup>7</sup>

This effect is specific to AZBN and should not apply to the dissociation of pentaphenylethane (PPE) which was investigated as the second substance. The use of iodine to measure the rate of this type of dissociation was first introduced by Ziegler, Ewald and Orth<sup>8</sup> and was widely used by Bachmann.<sup>9</sup> Since the formation of triphenylmethyl iodide in this reaction with iodine is reversible these workers found it necessary to introduce pyridine and ethanol to react further with the iodide. In the present investigation the need for this was avoided by using a large excess of PPE and following only the first few percent of the dissociation, in the manner of Bawn and Mellish.<sup>10</sup> The dissociation of PPE was measured in toluene at 70° C and at pressures up to 1500 atm.

The third system investigated was the equilibrium between nitrogen tetroxide and nitrogen dioxide in carbon tetrachloride solution. This equilibrium was measured at 22° and 51.5° C and at pressures up to 1500 atm.