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HYDROGEN-ATOM TRANSFER REACTIONS AT HIGH PRESSURES

THE REACTION BETWEEN MERCAPTANS AND DIPHENYLPICRYLHYDRAZYL

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The rate of transfer of hydrogen atoms from mercaptans to diphenylpicrylhydrazyl (DPPH) has been investigated at pressures up to 10,000 atm. The reaction is considered as a simple analogue to chain transfer reactions occurring in polymerizing systems, and the results show it to be accelerated about 5-fold at 2700 atm for normal mercaptans, and about 20-fold for tertiary mercaptans.

The action of hydrostatic pressure in accelerating liquid-phase vinyl polymerizations has received considerable attention in recent years. The work of Norrish and his collaborators^{1, 2} and of Walling and Pellon³ on styrene in particular has done much to distinguish the effects of pressure on the separate steps of the polymerization process. Most of this knowledge is derived from detailed analysis of the whole process but some steps have also been investigated separately, either directly or by means of analogous simple reactions.

The effect of pressure on the production of free radicals from initiator molecules has been measured directly^{2, 3, 4} and the rate has been found to be retarded between 1.3- and 1.6-fold at 1500 atm.

The addition of an initiating free radical to a monomer molecule can be compared with the iodine-catalyzed isomerization of dichlorethylene in which the rate-determining step is the addition of an iodine atom to the double bond. This reaction has been found to be approximately twice as fast at 3000 atm as at atmospheric pressure.⁵ The rate of the propagation reaction, which has the same mechanism of radical addition to a double bond, has been found to be accelerated six-fold at 3000 atm with styrene.² The large acceleration in this case has been attributed to the ordering effect of pressure on the monomer.

It is usually assumed that the bimolecular transfer reaction is accelerated by pressure to about the same extent as the propagation reaction and this assumption leads to equations^{2, 3} which qualitatively predict the observed change of molecular weight with pressure.

The present investigation was undertaken in order to obtain some direct information about the effect of pressure on transfer reactions by studying a model reaction. The abstraction of a hydrogen atom from a mercaptan,



is a typical transfer reaction which is often used to control polymerization processes. A convenient free radical to use in this reaction is diphenylpicrylhydrazyl (DPPH), as it is stable, easy to handle, and its concentration can readily be measured