

KINETIC EVIDENCE FOR A BIMOLECULAR REACTION OF
2,2-DIPHENYL-1-PICRYLHYDRAZYL WITH PEROXYBENZOIC ACID

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Peroxybenzoic acid decomposes in various solvents through a radical chain mechanism involving an initial homolysis of the oxygen-oxygen bond (1). It seems of interest to measure the rate of this homolysis by the use of a suitable radical scavenger. In fact, 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been used for such a purpose with peroxybenzoic acid by Cohen and Edwards (2) and with peroxyauric acid by Vorobiev, Lefort, Sorba and Rouillard (3). These two groups of workers assumed a unimolecular decomposition of these peroxy-acids in the presence of DPPH, because the rate of disappearance of DPPH was independent of its concentration and of the first order in the concentration of a peroxy-acid. 2,2-Diphenyl-1-picryl-hydrazyl, however, has now been found to be inadequate as a scavenger, since it reacts bimolecularly with peroxybenzoic acid, as has been shown by the following experiments.

A large excess of peroxybenzoic acid (10^{-1} - 10^{-2} mole/l.) was allowed to decompose in 1,2-dichloroethane in the presence of DPPH (10^{-2} - 5×10^{-5} mole/l.) at 55 and 65°C under an

atmosphere of nitrogen until most of DPPH had been consumed. Aliquots were withdrawn from the reaction mixture at known times, chilled to stop the reaction, and appropriately diluted with 1,2-dichloroethane, and the optical density of the diluted solutions was measured at $530\text{ m}\mu$, i.e., the absorption maximum of DPPH in this solvent, with a Hitachi EPS-2U spectrophotometer. Control experiments showed that peroxybenzoic acid, in the absence of DPPH, scarcely decomposed under otherwise the same experimental conditions.

The measurements showed that, the logarithm of the concentration of DPPH, and not the concentration itself, decreased almost linearly with time, though, in some runs, it decreased a little more slowly in the later stage than in the earlier stage of the reaction. This fact clearly shows that, in the presence of an excess of peroxybenzoic acid, the rate of decrease of DPPH is of the pseudo-first order, at least in the early stage, with respect to the concentration of DPPH*, and therefore, the rates observed are approximately represented by

$$-d[\text{DPPH}]/dt = k[\text{DPPH}].$$

Pseudo-first order rate constants (k) calculated from the initial reaction rate with the same initial concentration of peroxybenzoic acid were found to be nearly constant, e.g., 2.18, 2.33 and $2.56 \times 10^{-4}\text{ sec.}^{-1}$ at 65°C for the initial concentration of DPPH of 4.23×10^{-3} , 7.96×10^{-4} and 5.39×10^{-5} mole/l., respectively, that of peroxybenzoic acid

* A similar dependence of the rate on the concentration of DPPH was also observed in the reaction in benzene at 50° and 70°C , though detailed analysis of the rate data were not made.

being 0.956×10^{-1} mole/l. Since the pseudo-first order rate constants were found to be approximately proportional to the initial concentration of peroxybenzoic acid, the rate law obeys the following expression:

$$-d[\text{DPPH}]/dt = k_2 [\text{C}_6\text{H}_5\text{CO}_2\text{H}][\text{DPPH}]$$

The mean values of the bimolecular rate constants (k_2) obtained are 1.61×10^{-3} at 55° and 2.31×10^{-3} mole $^{-1}$ l. sec. $^{-1}$ at 65°C , the activation energy being about 8 kcal./mole.

It is now clear that peroxybenzoic acid reacts with DPPH predominantly in a bimolecular way, although further detailed analysis of the complete kinetic behaviour has not yet been attempted, because the complex nature of this reaction is evident. In fact, there are indications that unstable products are involved which may bring about the complexity of kinetics. The fact that 1,1-diphenyl-2-picrylhydrazine is readily oxidized by peroxybenzoic acid to DPPH even at room temperature, as shown by a separate experiment, suggests that a hydrazine-type compound, which is often inferred to be the product originating from DPPH (4), if formed at all in the present experiment, may be reoxidized to the hydrazyl-type radical, adding to the complexity of the kinetic behaviour. The observation that, during the reaction, a new absorption maximum, the origin of which is not identified, appeared at about $390 \text{ m}\mu$ and then gradually disappeared may have some connection with the above reoxidation process.

References

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