

Decomposition of Organic Peroxides

CONTINUING the investigation on the alkyl peroxides¹ and their relation to combustion phenomena, we have now obtained data on ethyl hydrogen peroxide, and propyl hydrogen peroxide.

Ethyl hydrogen peroxide decomposes heterogeneously in the temperature range 140–200°, the rate of reaction being in accord with the expression for adsorption derived from the Langmuir isotherm, due allowance being made for the buffering effect of unchanged peroxide and decomposition products. In agreement with this result, packing the vessel greatly increases reaction rate. It was also found that coating the surface with salt increases the reaction rate, which may be connected with the suppressing effect of salted walls on the reactions of hydrocarbon and oxygen. The products of the peroxide are mostly liquid at room temperature and include acetaldehyde and formaldehyde.

At higher pressures the decomposition is homogeneous, explosive, and is attended with light emission. The products of the decomposition are chiefly gaseous, and resemble those obtained from explosion of the mixture $C_2H_6 + O_2$.

Propyl hydrogen peroxide was not obtained pure, but the preparation used (60 per cent by iodometric method) formed propionaldehyde on heating at 200°, together with a gas containing propylene, ethylene, methane, hydrogen and carbon monoxide. No explosive decomposition has yet been observed.

Both the above compounds initiate markedly the slow reaction $C_3H_8 + O_2$; although they were found to reduce the induction period, they did not, however, affect the subsequent reaction rate; that is, in the expression $\omega = A(e^{\phi t} - 1)$, only A , and not ϕ is changed.

Their initiating effect can be nullified by poisoning (for example, with salt) the surface of the reaction vessel, which leads to the conclusion that the initiation takes place *after* a collision of the peroxide with the wall, which can direct the decomposition in two senses:

(i) peroxide \rightarrow initiators,
clean wall

or (ii) peroxide \rightarrow inert products,
poisoned wall

This conclusion is in agreement with deductions from the observed accelerating effect of inert gases on the reaction $C_3H_8 + O_2$, for if the first reaction product is a peroxide, the reaction:

(iii) peroxide + fuel \rightarrow chain carrier,
(in gas)

will be favoured at the expense of reaction (ii). A possible alternative explanation of the effect of the inert gas would be that it is more adsorbed on the poisoned surface than on the clean surface.

To settle this point, further experiments on the effect of inert gases on the decomposition of these peroxides are in hand.

It is noteworthy that hydrogen does not accelerate the slow oxidation of propane.

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Mechanism of the Rearrangement of Phenyl Ethers

WHEN certain phenyl ethers are heated at their boiling points, the non-aromatic group migrates from the oxygen to the nucleus. The more important groups which so migrate are allyl, benzyl and *tert.*-alkyl. If the rearrangement of some of these ethers is effected in a suitable solvent, the migrating group is transferred, in part, to the solvent. Thus by heating a quinoline solution of benzylphenyl ether, benzyl quinoline is formed together with the normal products of the rearrangement. Toluene is also formed.

These observations find a satisfactory explanation if the assumption be made that the preliminary phase of the rearrangement is the elimination of the migrating group as a free radical. Thus toluene results from the disproportionation of the benzyl radical—a reaction known to occur with free radicals¹. The transference of the migrating group to the solvent arises out of its reaction with the free radical. The assumption that free radicals take part in the reaction makes clear the observation, hitherto inexplicable, that the rearrangement of benzylphenyl ether is very materially assisted by the presence of metals such as zinc or copper².

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¹ Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

² Belhagel and Freilensehner, *Ber.*, **67**, 1368 (1934).

Splitting of the Hæmocyanin Molecule by Ultra-violet Light

INVESTIGATIONS along different lines (ultracentrifugal sedimentation¹, X-ray analysis²) have shown that the proteins contain particles possessing the hall-mark of individuality and therefore are, in reality, giant molecules. We have good reason to believe that the particles in protein solutions and protein crystals are built up according to a plan which makes every atom in it indispensable for the completion of the structure. Primary protein reactions are therefore elementary acts which must, of necessity, obey the laws of quantum mechanics³.

From this point of view, it would seem of interest to test the action of various energy quanta on proteins under such conditions that complications by secondary reactions are reduced to a minimum. The experience with protein dissociation reactions accumulated in this laboratory¹ indicates that the forces holding the large blocks of very big molecules together are less strong than the forces acting between the dissociable parts of smaller protein molecules. The chance of observing the primary process caused by the absorption of an energy quantum, therefore, appears to be most favourable in the case of proteins of very high molecular weight.

We accordingly chose the hæmocyanin of *Helix pomatia* (molecular weight 6,740,000) as protein material for our first experiments. Splitting of this molecule by ultra-sonic waves has recently been observed in this laboratory⁴. As energy quanta, we used ultra-violet light. Hæmocyanin solutions of various pH were exposed to the radiation of a quartz mercury lamp. By means of ultracentrifugal sedimentation determinations, it was found that at a pH of 6.2 a splitting into half-molecules occurs. Prolonged irradiation causes denaturation, finally resulting in complete precipitation. It is of interest

¹ NATURE, **141**, 472 (1938).