Tetrahedron Letters No.14, pp. 1-4, 1960. Pergamon Press Ltd. Printed in Great Britain.

THE REACTION OF OZONE WITH ORGANIC HYDROPEROXIDES

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(Received 22 March 1960; in revised form 25 April 1960)

OZONE and hydrogen peroxide are known to react with mutual deoxygenation and Taube and Bray[1] have demonstrated that a free radical chain process is involved with initiation by:-

$$H_2O_2 + O_3 \longrightarrow HO_2\cdot + HO\cdot + O_2$$

Organic hydroperoxides have now been shown to be destroyed by ozone in what is apparently a similar deoxygenation reaction. t-Butyl hydroperoxide, which gave the minimum of side reactions, was chosen for detailed study and Fig. 1 illustrates the ozone uptake curve for this peroxide in carbon tetrachloride solution at -25°. After ozone absorption had virtually ceased the colourless solution, in which droplets of water were visible, contained no peroxidic material reducible by stannous chloride. Analysis of the solution, after drying, by both infra-red spectrophotometry and gas-liquid chromatography (stationary phase dinonyl sebacate on acid-washed celite) gave results in excellent quantitative agreement. The major product was t-butanol accompanied by acetone and di-t-butyl peroxide. G.L.C. indicated the presence of only

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[1] H. Taube and W.C. Bray, J. Amer. Chem. Soc. 62, 3357 (1940).

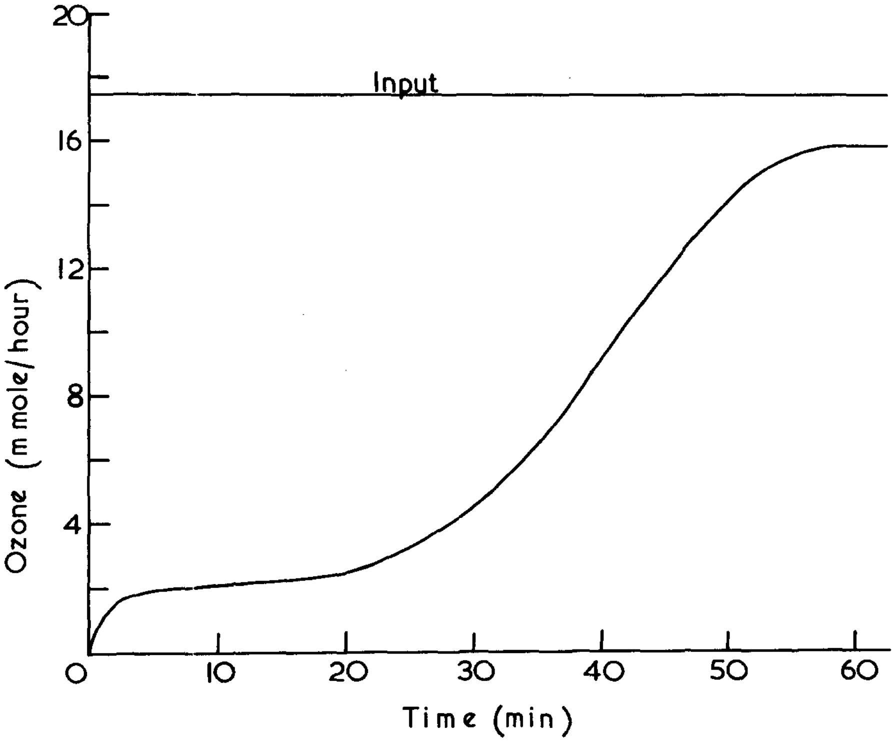

FIG. 1. Ozonolysis of Bu^tOOH (1.5 g) in CCl_4 (50 ml) at -25°C.

two other components, t-butyl chloride and a trace amount of an unidentified material. Table 1 shows the stoicheiometry of the reaction, water being independently estimated by the Karl Fischer technique.

TABLE 1

Products from the reaction of t-butyl hydroperoxide (1 mole) with ozone (0.51 mole)

Product	Bu^tOH	Bu^tOOBu^t	CH_3COCH_3	Bu^tCl	H_2O
Yield (mole)	0.68	0.079	0.10	0.042	0.264

Of the original t-butyl groups 98 per cent are thus accounted for (acetone $\equiv$ Bu^tO) but the active hydrogen balance is high (1.2 g atom) suggesting that part of the water has been derived by the further oxidation of t-butanol. Neither the products, nor their relative amounts, were altered significantly by changes in the ozone concentration or reaction temperature, although in very dilute ozone streams, loss of butanol and acetone in the effluent gas became noticeable.

Since carbon tetrachloride is stable to ozone under the reaction conditions but is readily attacked by reactive free radicals the formation of t-butyl chloride, which must result directly or indirectly from attack on solvent, implies that the ozone-hydroperoxide reaction involves such radicals. A reaction scheme, based largely on analogy with the hydrogen peroxide system, may therefore be postulated to account for the primary products observed, if not for their relative amounts.

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\begin{array}{lcccccccc}
ROOH & + & O_3 & \longrightarrow & RO_2\cdot & + & HO\cdot & + & O_2 \\
HO\cdot & + & ROOH & \longrightarrow & RO_2\cdot & + & \underline{H_2O} & & \\
RO_2\cdot & + & O_3 & \longrightarrow & RO\cdot & + & 2O_2 & & \\
RO\cdot & + & ROOH & \longrightarrow & \underline{ROH} & + & RO_2\cdot & & \\
 & & 2\,RO_2\cdot & \longrightarrow & \underline{ROOR} & + & O_2 & &
\end{array}
$$

As would be expected from this picture hydrocarbons used as solvent were extensively attacked. Thus a solution of t-butyl hydroperoxide in n-pentane absorbed many times more ozone than in carbon tetrachloride while the peroxide content decreased only slowly. This suggests an almost self-sustaining reaction in which hydroperoxide is generated by the radical-induced peroxidation of the solvent at approximately the same rate as it is destroyed by ozone. If the ozonolysis were continued the n-pentane eventually became miscible with water. With cyclohexane as solvent cyclohexanone and adipic acid were identified as products of a similarly catalysed oxidation.

Hydroperoxides other than t-butyl, e.g. tetralyl and cyclohexyl, were similarly destroyed by ozone but apparently underwent a general radical attack at the same time to give highly oxygenated and complex products. Perbenzoic acid, as an example of an acyl hydroperoxide, was found to be stable to ozone at both -25° and 20° in carbon tetrachloride solution.

Ozone is well known to catalyse the autoxidation of hydrocarbons, presumably via hydrogen abstraction by atomic oxygen, and it might therefore be expected that subsequent interaction of ozone with the derived hydroperoxide or peroxy radicals would occur. It may be significant that Schubert and Pease[2] report that the major product of the interaction of isobutane with ozonized oxygen at 28° is t-butanol accompanied by a trace of acetone. A more surprising observation in view of the present results is that of Rindtorff and Schmitt,[3] who obtained cumyl hydroperoxide by the ozonization of cumene.

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[2] C.C. Schubert and R.N. Pease, J. Chem. Phys. 24, 919 (1956).

[3] E. Rindtorff and K. Schmitt, Belg. Pat. 514, 128 (1952).