
Communications TO THE EDITOR

A Modification of Free Radical Reactions

Sir:

It has been observed that certain additives modify the course of free radical reactions. In the present communication we wish to describe the marked effect of trace amount of copper salts on both the rates and products of well known free radical reactions.

In the presence of 1 mole % of copper chloride benzoyl peroxide, *tert*-butyl peroxide, *tert*-butyl perbenzoate,¹ *tert*-butyl hydroperoxide, and α -cumyl hydroperoxide undergo a fast induced decomposition in solvents, whereas in the absence of copper chloride, these compounds normally undergo a slow first-order decomposition or no decomposition whatever. The products of the regular (R) and modified (M) reactions are quite different as illustrated in the following examples:

Decomposition of *tert*-butyl peroxide (1 mole) in benzaldehyde (7 moles) at 140°: (M) *tert*-butyl benzoate, 83%; benzpinacol dibenzoate, less than 5%. (R) only benzpinacol dibenzoate.²

Decomposition of benzoyl peroxide (1 mole) in cumene (10 moles) at 80°: (M) α -cumyl benzoate, 30% (b.p. 110°/0.1 mm., n_D^{20} 15560. *Anal.* Calcd. for C₁₆H₁₆O₂: C, 79.97; H, 6.7. Found: C, 80.15; H, 6.9. The infrared spectrum and the hydrolysis products are in agreement with the structure proposed); isopropyl biphenyls, 20%; no dicumene. (R) dicumene, 35%; isopropyl biphenyls, 24%.³

Decomposition of *tert*-butyl perbenzoate (1 mole) in cumene (10 moles) at 90° (perbenzoate was added dropwise to the cumene containing 0.01 mole of copper chloride): (M) α -cumyl benzoate, 40%.

Decomposition of benzoyl peroxide (1 mole) in octene-1 (8 moles) at 90°: (M) high mol. wt. polymers, 7 g; benzoic acid 72%; phenyloctene, 8%; 1:1 adduct (one benzoyloxy to one octene), 35%; 1:2 adduct, 34%. The 1:1 adduct is mostly 1-benzoyloxy octene-2, mixed with benzoyloxyoctane and 3-benzoyloxy-1-octene. It is unsaturated to the extent of 77%. Its infrared spectrum has a strong band at 975 cm.⁻¹ (trans double bond) and a weaker band at 930 cm.⁻¹ (established to be characteristic of terminal double bonds in this type of compounds). (R) polymers, 340 g. (average mol. wt., 600); benzoic acid, less than 6%.

(1) A separate investigation of the copper-catalyzed decomposition of *tert*-butyl perbenzoate by M. S. Kharasch and G. Sosnowsky is in press.

(2) F. F. Rust, F. H. Seubold, and W. E. Vaughn, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

(3) D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956).

Decomposition of benzoyl peroxide (1 mole) in octene-2 (8 moles) at 90°: (M) 1:1 adduct, 80% (completely unsaturated); only traces of higher polymers. (R) 1:1 adduct, 85% (only 60% unsaturated); 1:2 adduct, 13%.

Decomposition of benzoyl peroxide (1 mole) in a solution of valeraldehyde (2 moles) in carbon tetrachloride: (M) benzoic acid, one mole, acid anhydrides, one mole; no attack on carbon tetrachloride. (R) chloroform, 1 mole; hydrochloric acid, 1 mole; acid anhydrides, 2 moles (due to the reaction between the initially formed acid chloride and benzoic acid).⁴

Pyrolysis of dicumene in bromobenzene at 250°: (M) 70% of dicumene is recovered unchanged after 20 hr. (R) all the dicumene disproportionates into cumene and α -methylstyrene.

We wish to propose the formation of unstable copper organic complexes as intermediates in these reactions.

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(4) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.* **69**, 2916 (1947).

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A New Method of Introducing Peroxy Groups into Organic Molecules

Sir:

We wish to report the discovery of a new reaction. We find that in the presence of trace amounts of copper, cobaltous or manganous salts, alkyl and aralkyl hydroperoxides react readily with organic molecules containing a slightly activated hydrogen, replacing it with a peroxy group.¹ For example, *tert*-butyl hydroperoxide reacts with cumene in the presence of a metal salt to give *tert*-butyl- α -cumyl peroxide. This method appears as effective in introducing a peroxy group as *N*-bromosuccinimide is in

(1) W. Pritzkow and K. A. Muller [*Ann.*, **597**, 167 (1956) and *Ber.*, **89**, 2321 (1956)] are the most recent to report that Cu, Co, and Mn salts catalyze the decomposition of hydroperoxides. But neither they, nor any previous author, reported any peroxides among the products.