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SOME OBSERVATIONS CONCERNING THE COPPER SALT CATALYZED REACTIONS OF t-BUTYL PERBENZOATE WITH OLEFINS[1]

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IT has been reported[2-5] that catalytic amounts of certain transition metal salts can markedly modify the course of many reactions of organic peroxides with a wide variety of organic substances. One of the most interesting reactions found was that between olefins and t-butyl peresters in the presence of copper or cobalt salts.[2,6] The reaction has been reported to be specific, i.e. only one product, the 3-substituted olefin, is formed from

$$R\text{-}CH\text{=}CH_2 + C_6H_5CO_3C(CH_3)_3 \xrightarrow[\text{Salt}]{\text{Cu}} \underset{\displaystyle O_2CC_6H_5}{R\text{-}CH}\text{-}CH\text{=}CH_2 + (CH_3)_3COH$$

terminal olefins.[2,6] These findings have now been corroborated, since

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[1] Supported by the Alfred P. Sloan Foundation and the Colgate-Palmolive Company.

[2] M. S. Kharasch and G. Sosnovsky, *J. Amer. Chem. Soc.* **80**, 756 (1958).

[3] M. S. Kharasch and G. Sosnovsky, *Abstracts of Papers presented at the 134th Meeting of the American Chemical Soc.*, Chicago, September 1958, p. 7P.

[4] M. S. Kharasch and A. Fono, *J. Org. Chem.* **23**,324 (1958).

[5] M. S. Kharasch and A. Fono, *J. Org. Chem.* **24**, 606 (1958).

[6] M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Amer. Chem. Soc.* In press.

allylbenzene gave no cinnamyl benzoate. Of equal importance is the finding that propenylbenzene gave only cinnamyl benzoate. Thus, the two isomeric olefins yielded unrearranged products. These experiments show that these materials do not form a common intermediate, such as an allyl radical, carbonium ion or carbanion during the reaction. The evidence that these reactions are modified radical reactions is mainly circumstantial.[5] However, it is all reasonable.

The reaction of cyclohexene and t-butyl perbenzoate-carbonyl-O^{18} in the presence of cupric ion afforded cyclohexenyl benzoate, which was reduced (H_2/Pd) to cyclohexyl benzoate, which in turn was reduced (LAH) to cyclohexanol and benzyl alcohol. The oxygen-18 analytical data showed that the label was completely equilibrated between the two oxygens of the cyclohexenyl benzoate. The equilibration must have occurred during the formation of the unsaturated ester, since equilibration after its formation would necessarily lead to a mixture of allylic isomers. Any mechanism which does not permit equilibration is excluded. Such mechanisms are in general those which involve a concerted reaction of perester, olefin and catalyst.

The reaction of 3-deuterio-3-phenylpropene with t-butyl perbenzoate in the presence of cupric ion at 90° followed by deuterium analysis of the product showed that the isotope effect (k_H/k_D) for the hydrogen abstraction from the labeled allylbenzene was 4.3. The isotope effect is larger than one would predict for a simple hydrogen abstraction from allylbenzene by a t-butoxy radical. For example, Wiberg and Slaugh[7] have studied the deuterium isotope effects for the abstraction of hydrogen from toluene at 80° by several radicals. Their results are as follows: succinimide radical, 4.86; bromine atom, 4.59; and for the system ethylbenzene-succinimide radical, 2.67. One would predict that radical abstraction of hydrogen from allylbenzene would be more facile than from toluene or ethylbenzene. Therefore, for any given abstracting radical, allylbenzene would show the smallest isotope effect. The data in the literature concerning the reactivity of alkoxy radicals does not permit a quantitative comparison to that of a succinimide radical or bromine atom. All of the data[8,9] does indicate that a t-butoxy radical is more reactive than a succinimide radical. This being the case, the predicted isotope effect for the reaction of allylbenzene with a t-butoxy radical would be less than 2.67 and probably less than 2.0. One can conclude, therefore, with a high degree of certainty, that the hydrogen abstraction is not a simple reaction of a t-butoxy radical with allylbenzene. One also concludes this from the nature of the products obtained from isomeric olefins, since simple abstractions would give an allyl radical and ultimately lead to the same products from the isomeric olefins.

Although these data and the other available data[2,6] do not permit the postulation of a definitive mechanism, a satisfactory working hypothesis can be suggested. It is proposed that the copper ion reacts with t-butyl perbenzoate to give a complex of the copper ion with a t-butoxy radical and a benzoyloxy radical. This complex can co-ordinate with the olefin

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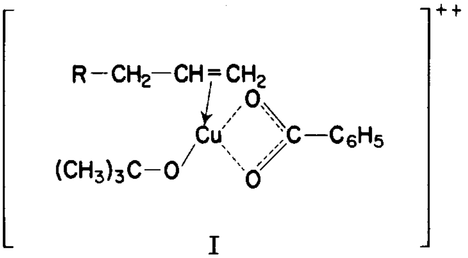
[7] K. B. Wiberg and L. H. Slaugh, J. Amer. Chem. Soc. **80**, 3033 (1958).

[8] C. Walling, B. Jacknow and W. Thaler, Abstracts of Papers presented at the 136th Meeting of the American Chemical Soc. Atlantic City, September, 1959, p. 54P.

[9] C. Walling, Free Radicals in Solution. John Wiley, New York (1957).

to give an intermediate (I), for which many resonance structures are available.



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Collapse of I can occur by hydrogen abstraction by the complexed t-butoxy radical which gives t-butyl alcohol and the appropriate complexed olefinic radical. Rapid combination within the copper complex of the olefinic radical and the benzoyloxy group leads to the product. This scheme accounts for the large isotope effect since the complexed t-butoxy radical will be less reactive than a free t-butoxy radical. One predicts that the complexed olefin will be less reactive towards hydrogen abstraction than the uncomplexed olefin. However, the overall rate may be greater because of a favourable entropy effect. Such a complex also accounts for the equilibration of the label in the benzoyloxy group and explains the fact that carbon dioxide is not formed when t-butyl peracetate is used, since a free acetoxyl radical loses carbon dioxide spontaneously.[10]

Further work is now in progress on these reactions. Of particular interest will be the outcome of a stereochemical study now in progress.[11]

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[10] Reference 9, p. 493.

[11] Prof. N. C. Yang, University of Chicago, private communication.