fer processes in mixtures of pyrimidines and purines will be published.

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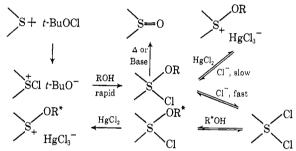
Pioneering Research Laboratory, U. S. Army Natick Laboratories Natick, Massachusetts 01760 Received June 10, 1969

Oxidation of Sulfides with *t*-Butyl Hypochlorite. Evidence for a Tetracovalent Sulfur Intermediate¹

Sir:

t-Butyl hypochlorite is an excellent reagent for the oxidation of sulfides to sulfoxides without concomitant formation of sulfones.² In certain cases, interesting and synthetically useful stereochemical control of such oxidations is possible.³ It has been proposed that alkoxysulfonium salts intervene in these oxidations:² such salts have been isolated after the addition of halide traps such as antimony pentachloride, mercuric chloride. or certain silver salts.⁴ Several papers have already appeared with mechanistic suggestions concerning such reactions.⁵ We now wish to report convincing evidence for the intervention of tetravalent sulfur species in such oxidations; we believe Scheme I describes the essential features of these reactions.

Scheme I



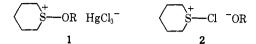
The hypochlorite oxidations are conducted at -78° . To thiane in methylene chloride was added 2 equiv of t-butyl hypochlorite followed by l equiv of mercuric chloride. Addition of ethyl ether caused the precipitation of the relatively unstable salt 1 (R = $t-C_4H_9$). The solid was rapidly analyzed by ir spectroscopy. A spectrum characteristic of a *t*-butoxysulfonium trichloromercurate was obtained. If ethanol (as little as 1 or 2 equiv) is present at the time of addition of the hypochlorite the principal product is salt 1 $(R = C_2H_5)$. On the other hand, if the ethanol is added after the addition of the *t*-butyl hypochlorite the salt obtained upon addition of mercuric chloride is again the *t*-butyl salt. The reaction of *t*-butyl hypochlorite in ethanol is much faster than the reaction of ethyl hypochlorite; therefore, we are confident that, in the former case, ethyl hypochlorite is not the effective reagent. These results led to the suggestion that the chlorosulfonium salt 2 is the first intermediate

(1) Part XX in the series Chemistry of Sulfoxides and Related Compounds. We gratefully acknowledge support by the National Science Foundation (Grant GP-8648).

(2) P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N
(3) C. R. Johnson and D. McCants, Jr., J. Amer. Chem. Soc., 87, 1109 (1965).

(4) C. R. Johnson and M. P. Jones, J. Org. Chem., 32, 2014 (1967).
(5) C. Walling and M. J. Mitz, *ibid.*, 32, 1286 (1967); L. Skattebøl, B. Boulette, and S. Solomon, ibid., 32, 3111 (1967).

along the reaction coordinate and that this chlorosulfonium salt reacts quickly even at -78° to give an alkoxy intermediate. This alkoxy intermediate could be an alkoxysulfonium chloride (which may or may not exist as a tight ion pair)⁶ or it could be a tetracovalent sulfur species. The evidence outlined below indicates the latter to be correct.



When alkoxysulfonium fluoroborates or trichloromercurates are dissolved in ethanol-1-14C, the rate of exchange is quite slow (less than 5% per hour) even at room temperature. However, when trace amounts of hydrogen chloride (added as a saturated solution in methylene chloride) are added, alkoxy exchange is rapid and statistical (based on total available alkoxy groups in the reaction system). Thiane was allowed to react with t-butyl hypochlorite in ethanol at -78° and the reaction mixture allowed to warm to room temperature over a 30-min period, followed by the addition of ethanol-1-14C. The mixture then was allowed to stir for an additional 30 min at room temperature. Mercuric chloride was added; 1-ethoxythioniacyclohexane trichloromercurate $(1, R = C_2H_5)$ was obtained at high yield and found to contain negligible radiolabel. These experiments indicate that the intermediate produced by the reaction of t-butyl hypochlorite and sulfide in alcohols has a relatively long lifetime even at room temperature and does not undergo rapid alkoxy interchange.

When the above reaction sequence was repeated, but with the addition of a catalytic amount of dry hydrogen chloride at the time of addition of the labeled ethanol, scrambling of the ethoxy group was found to be statistical after 15 min at room temperature. On the other hand, sulfuric acid does not catalyze the exchange, suggesting that catalysis is due to chloride ion rather than the acidity of hydrogen chloride. Salts such as tetra-n-butylammonium chloride are also effective catalysts. Apparently the trichloromercurate ion is not an effective source of halide ion under these conditions. Hydrogen chloride does not catalyze the exchange at -78°.

The observation that catalytic amounts of chloride ion catalyze exchange of alkoxysulfonium salts, coupled with the fact that the intermediate seems to be stable in the absence of chloride ion, leads to the suggestion that attack of chloride ion on the salt may be slow compared to subsequent steps leading to alkoxy interchange. If this were not true, small amounts of chloride ion would be rapidly consumed by the formation of the stable tetravalent intermediate and hence chloride ion in small amounts would not be an effective catalyst for statistical alkoxy exchange.

The nmr spectrum of the product of the reaction of methyl phenyl sulfide and t-butyl hypochlorite differs significantly from the spectrum of methylphenyl-tbutoxysulfonium fluoroborate. We do not anticipate that such differences could be entirely accounted for by ion-pairing phenomena and suggest that the data summarized in Table I provide additional evidence for a

⁽⁶⁾ For a recent discussion of tetracovalent sulfur intermediates and related ion pairs see H. Kwart, E. N. Givens, and C. J. Collins, J. Amer. Chem. Soc., 90, 7162 (1968).

Table I. Nmr Spectra in Methylene Chloride

Compound	Temp, °C	Δryl	es, ppm – S-Methyl	Alkoxy
OCH ₃				
C₀H₅SCH₃ BF₄⁻ +	37	7.85 (m)	3.43	3.86
O- <i>t</i> -C₄H₅ │ C₅H₅SCH₃ BF₄ [_]	-46	8.05 (2 H, m) 7.75 (3 H, m)	3.42	1.54
$\mathbf{O} - t - \mathbf{C}_4 \mathbf{H}_9$				
C₀H₅SCH₃ Cl	- 46	8.25 (2 H, m) 7.70 (3 H, m)	3.78	1.49

stable tetracovalent sulfur species. Owsley and Helmkamp⁷ have recently discussed evidence for a similar (9-chloro-9-methyl-9-thiabicyclo[6.1.0]intermediate nonane) formed by the nucleophilic addition of chloride ion to an episulfonium species.

(7) D. C. Owsley and G. K. Helmkamp, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 121.

(8) (a) Alfred P. Sloan Research Fellow, 1965-1968; (b) Fellow of the Economic Development Administration, Commonwealth of Puerto Rico.

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The Cage Recombination of Benzoyloxy Radicals: An Important Pathway in the Decomposition of Benzoyl Peroxide

Sir:

A recent report¹ that the decomposition of benzoyl peroxide is not accompanied by scrambling of carbonyl-18O label in recovered peroxide is surprising in view of the evidence²⁻⁴ for important amounts of such scrambling in the closely related reactions of acetyl peroxide. We wish to report experiments which show that scrambling of label by a radical-cage process does indeed occur for benzoyl peroxide.

Benzoyl-¹⁸O peroxide containing 1.36 atom label in the carbonyl was prepared by the method of Denney,⁵ and its decomposition was studied at 80° in 0.01 M solutions in isooctane and mineral oil. The demonstrated³ greater sensitivity of isotopic label determination by observation of the increase in peroxy oxygen label, rather than disappearance of carbonyl label, led us to use this technique. The acid hydrolysis of benzoyl peroxide to hydrogen peroxide was found to proceed too slowly to allow adoption of the published method in toto. We therefore devised a procedure in which t-butyl alcohol solutions of the solid residues left after removal of the solvent under reduced pressure (or after extraction with acetone, followed by removal of

(1) M. Kobayashi, H. Minato, and Y. Ogi, Bull. Chem. Soc. Jap., 41,

(1) M. Robartsin, M. Hanner, and J. C. Martin, J. Amer. Chem. Soc., 88, 3650
(2) J. W. Taylor and J. C. Martin, *ibid.*, 89, 6904 (1967).
(3) J. C. Martin and S. A. Dombchik, "Oxidation of Organic Com-

(3) J. C. Martin and S. A. Domotnik, "Ortration of Organic Con-pounds," Vol. I, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 269.
(4) S. A. Dombchik, Ph.D. Thesis, University of Illinois, 1969.
(5) D. B. Denney and D. Z. Denney, J. Amer. Chem. Soc., 79, 4806

(1957).

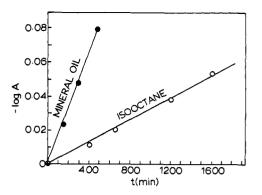


Figure 1. Scrambling of carbonyl-18O label in recovered benzoyl peroxide, measured by appearance of peroxide label in isooctane (closed circles) and mineral oil (open circles) at 80°.

the acetone under reduced pressure, in the mineral oil experiments) were treated with aqueous solutions of barium hydroxide. The analysis of the resulting oxygen for ¹⁸O content was accomplished with a Consolidated-Nier isotope ratio mass spectrometer. That indeed we were isolating oxygen from the peroxy oxygens was demonstrated by the observation that the oxygen derived from carbonyl-labeled peroxide before any thermolysis contained no label and that the use of water-18O as solvent for the generation of O₂ from the peroxide gave no introduction of label into the O_2 .

Figure 1 shows first-order rate plots for the scrambling of carbonyl label during decomposition in isooctane and mineral oil. The fraction of peroxide with specific carbonyl label is designated A (calculated from the excess of label in the carbonyl oxygen over that in the peroxide oxygen). At infinite time, equal labeling is expected in the oxygens and the fraction specifically labeled is zero. The kinetic scheme used for the analysis of the data is shown in Scheme I. The rate constants k_s for scrambling of the carbonyl label and k_d for disappearance of peroxide are given by $k_s = k_1 k_{-1}/k_1$ $(k_{-1} + k_p)$ and $k_d = k_1 k_p / (k_{-1} + k_p)$. Thus, k_d / k_s

Scheme I

$$R \xrightarrow{O^{*}} O \xrightarrow{O^{*}} R \xrightarrow{k_{1}} Q$$

$$[R \xrightarrow{O} O \xrightarrow{O} O \xrightarrow{O} R] \xrightarrow{k_{0}} products$$

$$k_{-1} \downarrow k_{1}$$
"scrambled peroxide"

 $= k_{\rm p}/k_{\rm -1}$, and the fraction of the benzoyloxy radicals recombining to form "scrambled" peroxide can easily be calculated. The rates for the over-all decomposition of the peroxide were followed by jodometric titration⁶ of solutions with 0.2 M styrene added to inhibit induced decomposition of the peroxide giving $k_{\rm d}$ = 2.70×10^{-5} sec⁻¹ in isooctane and 2.89×10^{-5} sec⁻¹ in mineral oil. (The determination of k_d in mineral oil is not very reliable. It is difficult to make sure that all induced decomposition is eliminated in so viscous a solvent. We therefore attach little significance to the indication that k_d is larger in mineral oil than in isooctane.)

(6) V. R. Kokatnur and M. Jelling, ibid., 63, 1432 (1941).