Recently, there has been some discussion as to whether enol or enolate intermediates and/or transition states are involved in NaOD–$D_2O$ and MeONa–MeOD catalyzed enolizations (4, 7, 8). Although the magnitude of the inductive effect alone of the carbonyl group is not known exactly, the magnitudes and the difference in the degrees of enhancement for the *exo* and *endo* exchange suggest that some conjugation does occur to the 1,3 carbonyl group to yield a delocalized species of the type **5**. Our data, therefore, give some support for an enolate-like transition state for enolization, at least in the dione system.

That *endo* exchange is enhanced more than *exo* may be a consequence of several factors. Since the degree of charge development should be less in the more reactant-like transition state for *exo* exchange, the demand for stabilization via delocalization and therefore sensitivity to the 1,3 carbonyl group would be less in the *exo* case. A possibility worthy of consideration is that the *exo* and *endo*-hydrogens in dione **2** are different conformationally[3] from those in **1**, so that homoenolic stabilization (13) is more facile for *endo* cleavage. Further studies on this and other 2,5-dione systems are presently underway.

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[3] That the 2,5-dione may exist in a twist conformation (cyclohexa-1,4-dione exists in a twist-boat conformation (9–12)) has been indicated by theoretical calculations and n.m.r. studies. An X-ray structure determination of the 2,5-dione is planned.

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# Interaction of *s*-butyl peroxy and alkoxy radicals

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Contrary to previous suggestions, the interactions of 2 *s*-butyl peroxy radicals yields no di-*s*-butyl peroxide. Di-*s*-butyl peroxide has been shown to result from mixing *s*-butyl hydroperoxide with oxalyl chloride, presumably via 2 *s*-butyoxy radicals produced in a solvent cage from homolysis of di-*s*-butyl peroxyoxalate formed *in situ*.

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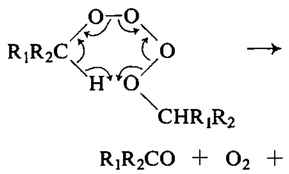
[1]



$R_1R_2CO + O_2 + R_1R_2CHOH$

The interaction of non-tertiary peroxy radicals has been suggested (1) to proceed via a rapid hydrogen transfer via a cyclic transition state available to tetroxides formed by these species, though not open to di-tertiary tetroxides, which yield alkoxy radicals and oxygen in a solvent cage (2). The extreme rapidity of, and kinetic isotope effects on *sec*-peroxy – *sec*-peroxy radical interaction tend to corroborate this supposition (3); however, the fact that $Co^{II}$-catalyzed decomposition of *s*-$BuO_2H$ yielded some 3% of *s*-$Bu_2O_2$ (4) has remained an obstacle, since for *t*-$BuO_2H$ + $Co^{II}$, the yield of *t*-$Bu_2O_2$ was entirely consistent with its being formed by interaction of 2 $t$-$\text{BuO}_2\cdot$'s, uninfluenced by the presence of metal ions (2, 4).

At the time that this was reported, we explained our inability to observe any $s$-$\text{Bu}_2\text{O}_2$ resulting from the solely free-radical-induced decomposition of $s$-$\text{BuO}_2\text{H}$ as an experimental difficulty in detecting small amounts of this substance (2). Now, having considerably more experience in analyzing for $s$-$\text{Bu}_2\text{O}_2$ by g.l.c. (5), we have repeated the decomposition of $s$-$\text{BuO}_2\text{H}$ by radicals produced from thermal decomposition of di-$t$-butyl peroxyoxalate (DBPO). Typically, 0.665 mmol of DBPO plus 1.22 mmol of $s$-$\text{BuO}_2\text{H}$ in 10 ml of benzene heated at 45 °C for 5 h gave 1.19 mmol of $t$-BuOH, 0.458 mmol of $s$-BuOH, and 0.549 mmol of butanone, as well as $\text{CO}_2$ and $\text{O}_2$. No $s$-$\text{Bu}_2\text{O}_2$ was found though as little as 0.002 mmol could have been readily detected by the g.l.c. analysis (5). It thus appears that free $s$-butyl peroxy radicals *do not* yield $s$-$\text{Bu}_2\text{O}_2$ on interaction.

The production of $s$-$\text{Bu}_2\text{O}_2$ when $s$-$\text{BuO}_2\text{H}$ is decomposed by $\text{Co}^{\text{II}}$ must therefore be influenced by the metal ion, possibly via an ion–radical complex having some oxonium-like character.

$$[2]\quad [s\text{-BuO}\cdot\text{Co}^{\text{II}}] \leftrightarrow [s\text{-BuO}^{+}\text{Co}^{\text{II}}] \xrightarrow{s\text{-BuO}_2\text{H}} s\text{-Bu}_2\text{O}_2 + [\text{Co}^{\text{III}}\text{OH}^{-}]$$

So far, of course, no one has demonstrated that two $s$-butoxy radicals if produced together in a solvent cage (*e.g.*, $2\ s\text{-BuO}_2\cdot \xrightarrow{?} [2\,s\text{-BuO}\cdot + \text{O}_2]$) would in fact combine to give $s$-$\text{Bu}_2\text{O}_2$, as well as diffusing apart or disproportionating the other choices open. While combination *vs.* diffusion has been examined for 2 $t$-$\text{BuO}\cdot$'s under various circumstances (6), for $s$-$\text{BuO}\cdot$'s, the difficulty has been to establish experimental conditions where the radicals are both generated pairwise, and recombination is observable (5).

We believe this has now been accomplished through attempts to synthesize di-$s$-butyl peroxyoxalate. Though $s$-butyl peroxyesters are known to be particularly labile (7), we had hoped that at very low temperatures the conditions used to prepare DBPO (8) (*i.e.*, hydroperoxide, oxalyl chloride, and pyridine) would work. However, as low as −50°, the major products using $s$-$\text{BuO}_2\text{H}$ were CO, $\text{CO}_2$, and butanone, with no evidence of free-radical-type products from the reactants or the solvent.

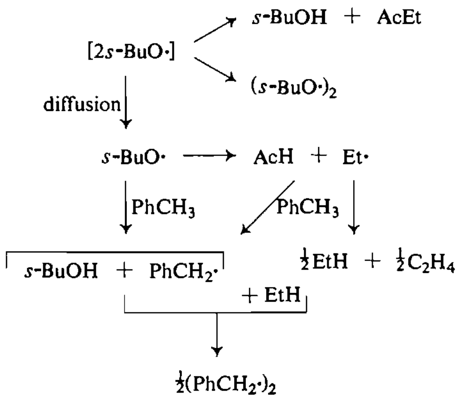
TABLE 1

Products from reacting 13.75 mmol of $s$-$\text{BuO}_2\text{H}$ with 7.0 mmol of oxalyl chloride in 20 ml of toluene at 0 °C

| Product | Amount, mmol | mol/mol of $s$-$\text{BuO}_2\text{H}$ |
|---|---|---|
| Acetaldehyde | 0.561 | 0.0408 |
| Butanone | 6.88 | 0.500 |
| $s$-BuOH | 3.67 | 0.267 |
| $s$-$\text{Bu}_2\text{O}_2$ | 0.018 | 0.0013 |
| Bibenzyl | 0.044 | 0.0032 |
| CO | 0.63 | 0.046 |
| $\text{CO}_2$ | 0.65 | 0.047 |
| $\text{O}_2$ | 0.038 | 0.0028 |
| $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ | 0.036 | 0.0026 |

Utilizing the method developed by Milas *et al.* (9) of using no pyridine, but removing evolved HCl by aspiration during the course of reaction, while not yielding any isolatable peroxalate, did result in products strongly suggestive of its formation (in low yield) and followed by homolysis. Table 1 shows those products identified by g.l.c. analysis from a typical run. The yield of conspicuously radical-type products is small, and it is not yet clear why the yield of acetaldehyde is not more nearly matched by that of bibenzyl (though, in the absence of contrary evidence, we are free to suggest that at this temperature, most ethyl radicals prefer to disproportionate, or to dimerize, rather than to abstract from toluene).

The obviously alternate route to $s$-$\text{Bu}_2\text{O}_2$, unreacted $s$-$\text{BuO}_2\text{H}$ + $s$-BuOH (or $s$-BuCl from $s$-BuOH + HCl) can be rejected on two grounds; (*1*), reactions of $\text{H}_2\text{O}_2$ or hydroperoxides with alcohols or alkyl chlorides is a classically bad way to prepare *sec*-alkyl peroxides; (*2*) in our experiments the presence of $s$-$\text{Bu}_2\text{O}_2$ was always



linked with the presence of bibenzyl, AcH, and $O_2$. Moreover, taking the yield of AcH as a fair approximation to the amount of *s*-butyl peroxyoxalate produced and decomposing homolytically, the yield of *s*-$Bu_2O_2$, $\sim 6\%$ of the initially produced caged radicals, is eminently reasonable in view of results with *t*-BuO· (2, 6).

Finally, the instability of *sec*-alkyl peroxyesters has been ascribed to concerted decomposition through a cyclic transition state, leading to ketone plus carboxylic acid (7). If this had been the case with di-*s*-butyl peroxyoxalate, a good yield of oxalic acid would be expected. In no case was oxalic acid found among the products, though it was shown to be stable under the conditions of reaction. While we yet have hopes of isolating di-*s*-butyl peroxyoxalate, we are, at the same time, exploring the reasons for our present failure; results to be published in due course.

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