difficulty encountered in the attempted formation of the *o*-tolyl spiro derivative is probably associated with the presence of both the *o*-methyl and the bridging N-alkyl groups.

An analogous silicon spiro compound [where R = $Si(CH_3)_3$] has been synthesized recently by Kummer and Rochow, who indicated that the presence of the N–$Si(CH_3)_3$ group was necessary for the formation of five-memberd rings by the reaction of chlorosilanes and ethylenediamines.[8] The present work shows that cyclic compounds can be obtained by the more general reactions 1 and 2 where R may be a variety of alkyl or aryl groups.

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It has come to our attention during the preparation of this note that the N-methyl and N-ethyl spirosilicon imidazolidines have been independently obtained through transamination by Dr. E. W. Abel and coworkers at the University of Bristol, England. We thank Dr. Abel for sharing his results with us.

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[8] D. Kummer and E. G. Rochow, *Z. anorg. allgem. Chem.*, **321**, 21 (1963).

CONTRIBUTION FROM THE METCALF RESEARCH LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND

An Isotope Study of the Decomposition of Caro's Acid

BY E. KOUBEK, GERRIT LEVEY, AND JOHN O. EDWARDS

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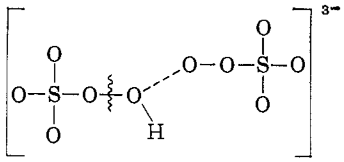
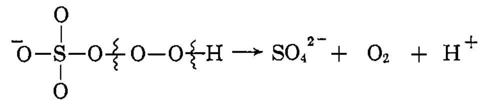
There has been considerable current interest in the mechanisms by which peroxides decompose. Ball and Edwards[1] reported a kinetic study on the aqueous decomposition of Caro's acid to give sulfate and oxygen. They suggested, on the basis of the rate law $R = k[HSO_5^-][SO_5^{2-}]$ and other evidence, a mechanism involving displacement on oxygen by oxygen involving an activated complex of the type



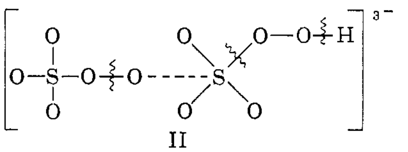
I

with dotted lines indicating bonds being formed and zigzag lines denoting bonds being broken. The intermediate HSO_6^- is presumed to decompose rapidly to oxygen, sulfate ion, and hydrogen ion.



$${}^{-}\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{S}}}-\text{O}\wr\text{O}-\text{O}\wr\text{H} \longrightarrow SO_4^{2-} + O_2 + H^+$$

Goodman, Robson, and Wilson[2] reported on a study of aromatic peroxy acid decomposition in aqueous solutions; they observed a rate law similar to the Caro's acid case, and they suggested a peroxy anion attack on the electrophilic carbonyl carbon of an un-ionized peroxy acid. They also suggested that this type of mechanism might hold for other peroxy acids including Caro's acid and this would involve (in its simplest form) an activated complex such as

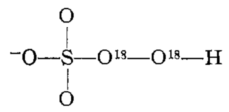


II

The original study[1] on Caro's acid has been repeated[3] and the alternative mechanism involving attack by peroxide oxygen on sulfur reiterated. Simultaneously, a study[4] of the decomposition of several peroxides was reported. Included were experiments involving double-labeled peroxyacetic acid, $CH_3C(=O)O^{18}O^{18}H$, in the presence of nonlabeled peroxyacetic acid; the results are consistent with a mechanism wherein a peroxyacetate ion attacks the carbonyl carbon of the un-ionized peroxy acid leading to an activated complex similar to type II.

In view of these observations and speculations, further study on the mechanism of the decomposition of Caro's acid seemed desirable. An experiment of the kind carried out earlier[4] using double-labeled peroxy acid was invoked in order to distinguish between the two suggested mechanisms (both of which are consistent with the rate law and other data) for the reaction between SO_5^{2-} and HSO_5^-. Mechanism I requires that one oxygen atom in each oxygen molecule originate from one peroxy anion; therefore, in the double-labeling experiment, scrambling of oxygen atoms is required and the O^{18} isotope will be predominantly in the O_2^{34} species. Mechanism II requires that both atoms in a product oxygen molecule come from the same peroxy anion so no scrambling is predicted; this was found to be the predominant (but not exclusive) product with peroxyacetic acid.[4]

We have now prepared a mixture of $KHSO_5$ species containing ~1.1% double-peroxide-oxygen-labeled $KHSO_5$



$${}^{-}\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{S}}}-\text{O}^{18}-\text{O}^{18}-\text{H}$$

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[1] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

[2] J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

[3] J. F. Goodman and P. Robson, *J. Chem. Soc.*, 2871 (1963).

[4] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).

and normal $KHSO_5$. Both the H_2O_2 used in preparing the labeled Caro's acid and the H_2O_2 obtained by acid hydrolysis of the $KHSO_5$ sample had the same amount of double labeling within experimental error. Therefore it is certain that the sample of $KHSO_5$ to be used in the decomposition runs was properly labeled (*i.e.*, no scrambling occurred during preparation) and that no peroxide oxygen exchange with solvent water occurs.

The data for three decomposition experiments (CO_3^{2-} I, CO_3^{2-} II, and HPO_4^{2-} are their symbols in Table I) are presented in Table I along with the comparative data for the H_2O_2 samples mentioned above. All data are given for the same mass spectrometer settings, and all of the decomposition solutions contained sufficient EDTA to eliminate trace metal catalysis; comparative kinetic runs with the same buffer solutions showed second-order kinetics as expected.[1-4] The first two samples were from decomposition runs carried out in carbonate at the pH of maximum decomposition rate[1]; the third sample, from a phosphate buffer, showed the expected lower rate but give otherwise identical results.

The data of Table I show, in the third column, the total atom per cent O^{18} in our samples of oxygen gas both from Caro's acid decomposition and from hydrogen peroxide. Since the values are the same within experimental error, exchange with solvent water either before, during, or after the decomposition is excluded. Since the value for O_2^{36} per cent is the same (see fourth line) both before formation of $KHSO_5$ and after hydrolysis, no scrambling occurs in the preparation of the sample to be decomposed.

TABLE I

ISOTOPE TRACER RESULTS FOR CARO'S ACID DECOMPOSITION

Sample	pH	Atom % O^{18}	O_2^{36}, %
CO_3^{-2} I[a]	9.4	1.42 ± 0.01	0.09 ± 0.02
CO_3^{-2} II	9.4	1.38	0.12
PO_4^{2-}[a]	7.4	1.44 ± 0.01	0.10 ± 0.02
H_2O_2[b]	...	1.44 ± 0.05	1.08 ± 0.02

[a] Average of two mass spectrometer runs. [b] Average of four samples (eight mass spectrometer runs): two samples by ceric ion oxidation of H_2O_2 used in preparation of Caro's acid and two samples obtained by hydrolysis of Caro's acid followed by ceric ion oxidation. The validity of such check experiments has been previously demonstrated: C. A. Bunton and D. R. Llewellyn, *Research*, **5**, 142 (1952); M. Anbar, *J. Am. Chem. Soc.*, **83**, 2031 (1961).

If complete scrambling during decomposition had occurred, the values for O_2^{36} per cent for the first three entries in the column would be ~0.02%. If no scrambling had occurred, the values would be 1.08 ± 0.02% as observed for the hydrogen peroxide samples. The data of Table I show that the oxygen molecules which result from spontaneous decomposition of Caro's acid are predominantly (91 ± 2%), but not completely, scrambled. Therefore any mechanism such as II is eliminated by the results. The isotope tracer results obtained here are consistent with nucleophilic displacement on oxygen by oxygen; indeed our data are direct evidence that such a displacement can occur.

The observation that small amounts of peroxydisulfate ion[3] and hydrogen peroxide[5] are formed during the decomposition of HSO_5^- suggests that peroxide metathesis

$$2HSO_5^- \rightarrow S_2O_8^{2-} + H_2O_2$$

can occur to a small extent during the decomposition.

Depending on the nature of the peroxide, decomposition *via* displacement on oxygen by oxygen (as appears to be the predominant situation here) or decomposition *via* attack at some other electrophilic center (as in the case of the peroxyacetic acid decomposition[4]) may occur. Since in neither case did we observe 100% compliance with the predicted isotope distribution for a single mechanistic path, it seems reasonable to conclude that peroxide decompositions of this type involve two competing pathways having identical rate laws. For example, the fact that 9% of the activated complexes (over and above the statistical probability) led to doubly-labeled oxygen molecules in this study can be interpreted as being due to a small contribution of an activated complex involving peroxy anion attack on sulfur (mechanism II). We hope to be able to sort out the relative rates for these competing paths in the future.

Experimental

The mixture of double-labeled H_2O_2 and normal H_2O_2 was prepared as in the previous study.[4] The preparation of Caro's acid followed the procedure of Ball[1]; solid $KHSO_5$ was made from the acid by careful neutralization with $KHCO_3$ and rapid evaporation of water.[3] Other procedures followed those employed previously.[1,4]

In the initial step of the synthesis (reaction of double-labeled oxygen with metallic sodium), a small amount of oxygen exchange with the glass vessel apparently took place for we found some $H_2O^{16}O^{18}$ in our hydrogen peroxide samples. This did not affect our results, since it only involved a small and constant correction factor for each experiment.

Acknowledgments.—We wish to thank Dr. K. M. Ibne-Rasa for suggestions, Dr. G. O. Dudek of Harvard University for aid with the mass spectrometer, and the U. S. Atomic Energy Commission for financial aid.

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[5] G. Levey, unpublished results.

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Dimethyl(trifluoromethylthio)arsine and Related Compounds[1]

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It has recently been reported[2] that bis(trifluoromethyl) disulfide reacts with tetrafluorohydrazine on

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[1] This work was supported by the National Research Council of Canada.

[2] E. C. Stump and C. D. Padgett, *Inorg. Chem.*, **3**, 610 (1964).