Finally, some mention should be made of the properties of the betaines. These may be considered tertiary amine–sulfur trioxide addition compounds. The presence of three ethyl groups on nitrogen should lead to considerable B strain[3] in the complex and it is therefore not unexpected that the compound $CH_3(C_2H_5)_2\overset{+}{N}SO_3^-$ could not be prepared. Although it is possible to prepare $(C_2H_5)_3\overset{+}{N}SO_3^-$ from the tertiary amine and pyridiniumsulfur trioxide, it could not be prepared by rearrangement because side reactions predominate at the high temperature required. However, when the R groups are tied back as in the piperidine and pyrrolidine derivatives, the compounds are stable and the rearrangement of the corresponding sulfonates is observed. It appears that the groups on nitrogen in the ester play a greater role in determining the rate of rearrangement than does the nature of the migrating group on oxygen.

Experimental Section

In a typical ester preparation, methyl N-methyl-N-ethylsulfamate was prepared by treating ethylmethylamine[4] with sulfuryl chloride. The sulfamyl chloride was then stirred with a cyclohexane suspension of sodium methoxide. After filtering the NaCl, the solvent was evaporated and the ester distilled at 1 mm pressure. The corresponding betaine was prepared by method A. To 1.84 g of ethyldimethylamine in about 15 ml of H_2O, there was added 4 g of pyridiniumsulfur trioxide.[5] After about 10 min of shaking, the solid was separated and recrystallized from hot water, mp 135°. In a typical thermal rearrangment to betaine (method B), methyl N-piperidinesulfonate was heated under nitrogen at 130° for 20 min. After cooling, the crystals were washed with small quantities of ice water and, on drying, melted sharply at 104–105°. Attempted recrystallization from water or other solvents was unsuccessful.

(3) H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **75**, 16 (1953).
(4) J. Graymore, *J. Chem. Soc.*, 1490 (1931).
(5) H. H. Sisler and L. F. Audrieth, *Inorg. Syn.*, **2**, 173 (1946).

The Base-Catalyzed Decomposition of Peroxypivalic Acid in Aqueous Solution

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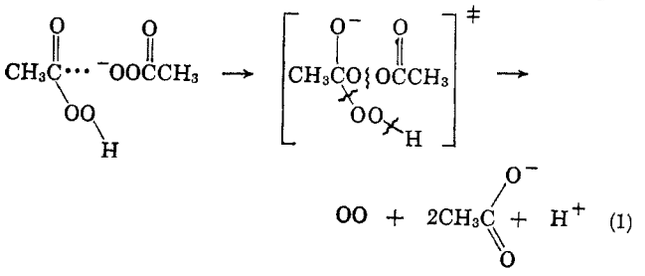
In an earlier paper,[1] it was suggested that the base-catalyzed decomposition of monosubstituted peroxyacids to parent acid and oxygen could proceed by at least two distinctly different mechanisms. For example, it appeared from kinetic and isotope-labeling experiments that both peroxyacetic and peroxychloroacetic acid[2] undergo decomposition *via* nucleophilic attack by the peroxy anion upon the carbonyl center of the peroxy acid leading to a transition state, as shown in eq 1.



(1)

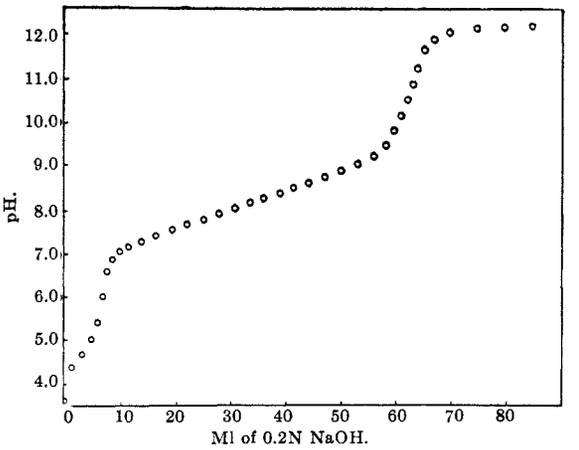
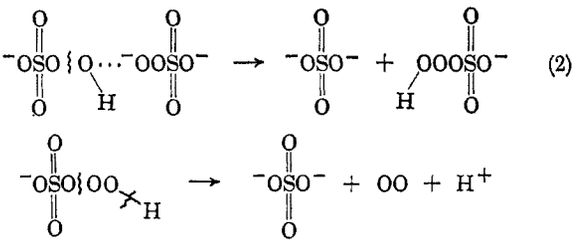


Figure 1.—Titration curve for peroxypivalic acid at 25°.

However, similar experiments upon peroxymonosulfuric acid[1] indicate that this compound undergoes decomposition mainly through nucleophilic attack by the peroxysulfate ion upon the outer peroxidic oxygen of the peroxybisulfate ion. This reaction is believed to lead to formation of the unstable intermediate (HSO_5^-), which rapidly decomposes to oxygen and bisulfate ion. (See eq 2.)



(2)

It was decided to further study this proposed duality of mechanisms by investigating the base-catalyzed decomposition of peroxypivalic acid. This particular compound was selected because of the well known steric effect of the *t*-butyl group upon reactions occurring at the carbonyl center.[3]

However, since the preparation of peroxypivalic acid could not be found in the literature, it was necessary to first develop a satisfactory synthesis. After several attempts we were successful in obtaining the desired compound in sufficient quantities to carry out our intended experiments. Figure 1 represents a typical titration curve of a sample of peroxypivalic acid. From this curve and several others, the pK_a of this new peroxy acid was determined to be 8.23 ± 0.03.

A study of the decomposition of this compound in carbonate buffer, containing appropriate amounts of EDTA, revealed that this peroxy acid also follows the generally observed decomposition pattern.[2,4,5] The rate of decomposition was found to be second order in total peroxide with a maximum at pH = pK_a = 8.23 (k_{obsd} = 3.4 × 10^{-3} l./mole sec at 25°). A summary of

(1) E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, **3**, 1331 (1964).
(2) 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).
(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1960, p 318. We have also observed that peroxyacetic acid undergoes acid hydrolysis eight to nine times faster than peroxypivalic acid.
(4) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).
(5) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

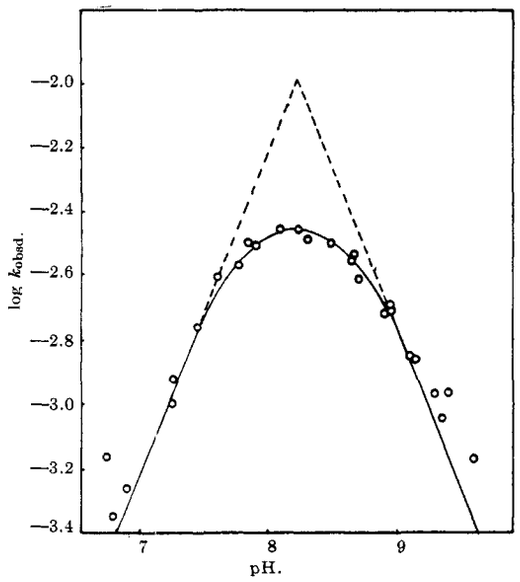


Figure 2.—Second-order rate constant for decomposition of peroxypivalic acid as a function of pH at 25.0°.

the results obtained are given in graphical form in Figure 2 in order to illustrate the pH dependence of the decomposition.

Once the general pattern of decomposition was established, the decomposition of a sample of peroxypivalic acid in which 1.2% of the peroxidic oxygen was doubly labeled in O^{18}, $(CH_3)_3C(=O)O^{18}O^{18}H$, was carried out. The oxygen gas evolved contained an amount of O_2^{36} consistent with 24% of the decomposition proceeding by attack on carbon (eq 1) and 76% attack on oxygen (eq 2). See Table I.

TABLE I

MASS SPECTROGRAPHIC ANALYSIS OF GAS SAMPLES FROM THE DECOMPOSITION OF DOUBLY LABELED PEROXYPIVALIC ACID

	Peak heights		
	O^{32}	O^{34}	O^{36}
I. H_2O_2[a]			
Oxygen	2100	16.4	25.9
Oxygen percentage	98.06	0.73	1.21
II. Peroxypivalic Acid[b]			
Oxygen	2150	57.2	6.4
Oxygen percentage	97.12	2.59	0.29

$$\% \text{ unscrambled} = \frac{0.29}{1.21} \times 100 = 24$$

[a] Oxygen liberated by ceric oxidation of H_2O_2 in perchloric acid solution.[2] [b] In carbonate buffer at pH 8.4.

Thus, we were able to alter the mechanism of decomposition by sterically hindering the carbonyl site of peroxyacetic acid, lending additional support to the original postulate of a dual mechanism.

When this investigation was near completion, Edwards and coworkers[6] reported a similar study using monoperoxyphthalic acid. Even though this compound is not as similar in nature to peroxyacetic acid as the one being reported here, the results appear to be in complete agreement.[7] As a matter of convenience, the results obtained on the systems studied to date are listed in Table II.

TABLE II

Monosubstituted peroxy acid	Attack on O_2, %[a]	Attack on C or S, %[a]
Peroxyacetic acid	17	83
Peroxysulfuric acid	90	10
Peroxyphthalic acid	74	26
Peroxypivalic acid	76	24

[a] Based on the results of doubly labeled isotope tracer experiments.

Experimental Section

The procedures used in the kinetic and labeling experiments have been previously reported.[1,2] Peroxypivalic acid was prepared in yields of up to 80% as follows. To 11.6 ml of concentrated sulfuric acid at 0°, 5.6 ml of pivalic acid (mp 34–35°) was slowly added. This was followed by 3.4 ml of deionized water which was in turn followed by 5.1 ml (dropwise) of 50% hydrogen peroxide. The resulting mixture was allowed to stand at 20° for 1 hr after which it was extracted with two 50-ml aliquots of methylene chloride. Removal of the methylene chloride by means of a water aspirator and a rotary evaporator left an oily residue which possessed a sharp odor characteristic of peroxycarboxylic acids. Analysis of the residue by both basic and iodimetric titration[8] confirmed that it contained only pivalic and peroxypivalic acids.

If this material is diluted with 25 ml of water and then brought to a pH of 6.2 with 3 *M* NaOH, extraction with two 50-ml portions of methylene chloride leads to a product of 95% purity.

Registry No.—Peroxypivalic acid, 14909-78-5.

Acknowledgments.—This work was supported in part by the Office of Naval Research. We also wish to thank Dr. Fred Saalfeld of the Naval Research Laboratories for the mass spectral analysis.

(6) R. E. Ball, J. O. Edwards, M. L. Haggett, and P. Jones, *J. Am. Chem. Soc.*, **89**, 2331 (1967).

(7) However, it may be noted that in the case of monoperoxyphthalic acid, in addition to sterically hindering the carbonyl center, attack may also be preferred at oxygen due to a loss of conjugation following attack on carbon. For this reason it is likely that benzoic acid[5] also undergoes decomposition *via* attack upon oxygen to a greater extent than that found for peroxyacetic acid.

(8) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

2,2′-Dihydroxydiphenyl Sulfone and Its Monoethers

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Because of a need for a quantity of very pure 2,2′-dihydroxydiphenyl sulfone (I), the synthetic methods reported in the literature were surveyed. The earliest work, that by Tassinari,[2] was misleading in that he believed he had prepared the 3,3′ isomer when in fact he had prepared I. Mauthner[3] prepared I by a somewhat different route, but his product was impure, as was demonstrated by Machek and Haas.[4] This previous work was summarized by Gump and Vitucci,[5]

(1) To whom requests for reprints should be addressed.
(2) G. Tassinari, *Gazz. Chim. Ital.*, **17**, 90 (1887); **19**, 343 (1889).
(3) F. Mauthner, *Ber.*, **39**, 1351 (1906).
(4) G. Machek and H. Haas, *J. Prakt. Chem.*, **160**, 41 (1942).
(5) W. Gump and J. Vitucci, *J. Am. Chem. Soc.*, **67**, 238 (1945).