

ANALYTICAL CHEMISTRY

1910

Studies in the Structure of Organic Peroxides

DANIEL SWERN and LEONARD S. SILBERT

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

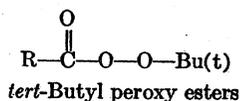
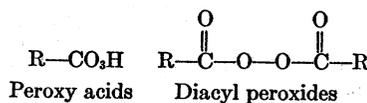
Studies in the Structure of Organic Peroxides

► Infrared, dipole moment, and molecular weight studies have shown that peroxy acids exist in solution exclusively as intramolecularly hydrogen-bonded monomers containing a puckered five-membered ring. In the solid state peroxy acids exist as dimers. Diacyl peroxides and *tert*-butyl peroxy esters also have a skewed structure in the peroxide grouping. Polarography permits the establishment of an order of stability of organic peroxides which parallels their energy of activation for thermal decomposition and reactivity with iodide ion.

WITHIN the past decade considerable information has been acquired on the structure of several important classes of organic peroxides, but the picture is not yet complete. Numerous approaches have been applied, both singly and in combination, to the elucidation of their structures, including, among many other techniques, analytical, spectral, polarographic, x-ray dif-

fraction, and dipole moment studies. The structural problems will inevitably be completely solved by such a broad approach using every physical and chemical tool available.

The major portion of this paper is devoted to the structure and properties of three important classes of organic peroxides: peroxy acids, diacyl peroxides, and *tert*-butyl peroxy esters:



ORGANIC PEROXY ACIDS, R-CO₂H

For many years, it has been known that peroxy acids contain one more oxygen atom than the corresponding carboxylic acids, but a reasonably exact structure of the peroxy-carboxyl group was evolved only within the past few years.

The first clue that there is a significant structural difference between peroxy acids and carboxylic acids was obtained in the period 1909-1912, when it was shown that peroxy acids have lower boiling points than the corresponding carboxylic acids in spite of the higher molecular weights of the former (16). This simple fact received its proper interpretation many years later by the infrared spectral work of Giguère and Olmos (4) and of Swern *et al.* (17), by the molecular weight and x-ray diffraction studies of the latter group (17), and by the dipole moment studies of Rittenhouse *et al.* (11).

Giguère and Olmos (4) studied the infrared spectra of peroxyformic and peroxyacetic acids in the vapor and liquid phases. Considering the instability of these two peroxy acids and the difficulties in handling them, the conclusions they arrived at were remarkably accurate. The development by Parker, Ricciuti, Ogg, and Swern (8) of an efficient synthetic method for the facile preparation of the relatively stable, crystalline C₆ and higher aliphatic peroxy

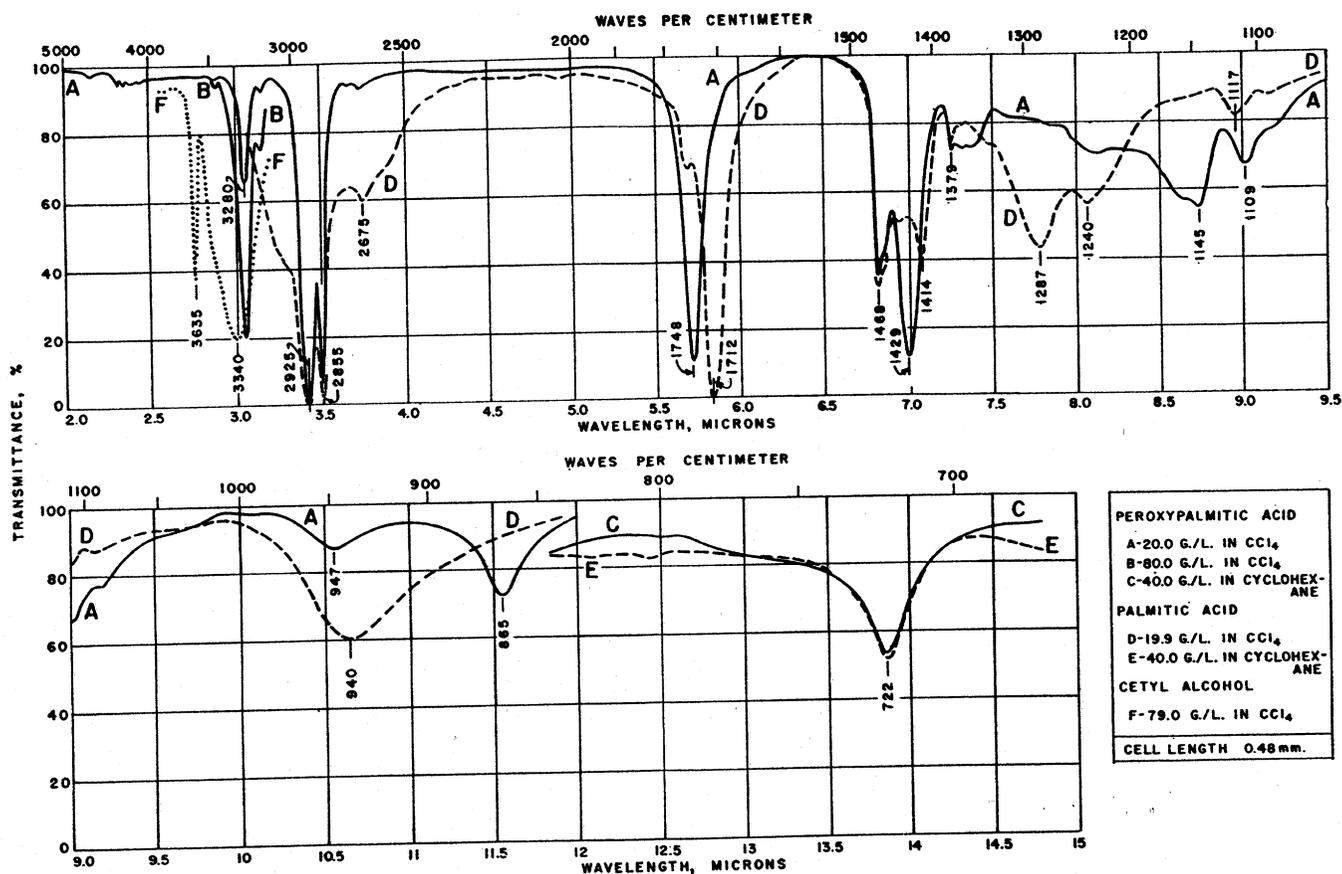


Figure 1. Infrared spectra of peroxyalmitic and palmitic acids and cetyl alcohol in carbon tetrachloride solution

acids, however, permitted a detailed study of the structure of these compounds by infrared, x-ray diffraction, molecular weight, and other techniques.

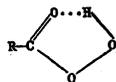
Infrared Spectra. In solution, the infrared spectra of C_6 to C_{16} aliphatic peroxy acids are substantially the same, showing only minor variations with chain length (17). Only three regions of the infrared spectra are discussed—the hydroxyl, the carbonyl, and the peroxide (O—O) regions.

HYDROXYL REGION. Figure 1 shows that the hydroxyl stretching vibration of the peroxy acids (curves A and B) is found at 3280 cm^{-1} (3.05 microns) in carbon tetrachloride. It is especially significant that the position of this band shows no change with dilution (0.3 to 0.006 mole per liter) and its absorptivity shows essentially no change.

The position of the hydroxyl band of peroxy acids compared to that of the unassociated fatty acid at 3530 cm^{-1} (2.83 microns) and of the unassociated fatty alcohol at 3635 cm^{-1} (2.75 microns) (curve F) shows that the peroxy acids are hydrogen-bonded. Further, the insensitivity of the band to dilution shows that the hydrogen bonding is intramolecular in solution.

Even at as low a concentration as 0.006M, peroxy acids show no unassociated hydroxyl band; only that

of associated hydroxyl is seen. The two-dimensional structure proposed by Giguère and Olmos (4) for peroxyacetic and peroxyformic acids is a reasonable two-dimensional one for the entire homologous series of aliphatic peroxy acids. The structure is shown below:



In the solid state, the hydroxyl band of the peroxy acids (Figure 2, A) is shifted to even lower frequencies (3200 cm^{-1}) (3.13 microns) and is broader than in solution. The broadening and larger shift of frequency suggest that in the solid state the peroxy acids, like the carboxylic acids, are intermolecularly hydrogen-bonded. (This point is discussed further under x-ray diffraction.)

In comparison, cetyl alcohol in the solid state (C) has its hydroxyl band at about 3250 cm^{-1} (3.1 microns) and palmitic acid (B) has the usual broad band centered roughly around 2900 cm^{-1} (3.4 microns). Thus, the hydroxyl band of the solid peroxy acids is between that of solid alcohols and carboxylic acids, but much nearer to that of alcohols. Solid peroxy acids, therefore, are slightly more strongly intermolecularly hydrogen-bonded than

are the solid alcohols but not nearly so strongly as the solid acids.

CARBONYL REGION. Peroxy acids have a strong, single carbonyl absorption band at 1747 to 1748 cm^{-1} (5.72 microns), both in solution (Figure 1, A) and in the solid state (Figure 2, A), although in the latter case, the band is slightly less sharp. On the other hand, carboxylic acids in solution have two carbonyl bands. One is a strong band at 1708 to 1712 cm^{-1} (5.85 to 5.84 microns) and the other is a weak band at about 1760 cm^{-1} (5.68 microns). The latter is attributed to the monomeric carbonyl group, and is not present in the solid state spectra.

In contrast, peroxy acids show no evidence of an unbonded carbonyl group under any conditions we have studied, which is in accord with the conclusion that they are completely chelated, as illustrated previously.

The shift of the carbonyl frequency in peroxy acids parallels the shift of the hydroxyl frequency. If one assumes that the frequency of an unbonded carbonyl would lie near 1760 cm^{-1} in peroxy acids, as it does in carboxylic acids, then the shift of the carbonyl of peroxy acids to 1747 to 1748 cm^{-1} (5.72 microns) on forming the chelate is less than the shift to 1705 to 1725 cm^{-1} (5.87 to 5.85 microns) in the carboxylic acid dimers. As with the

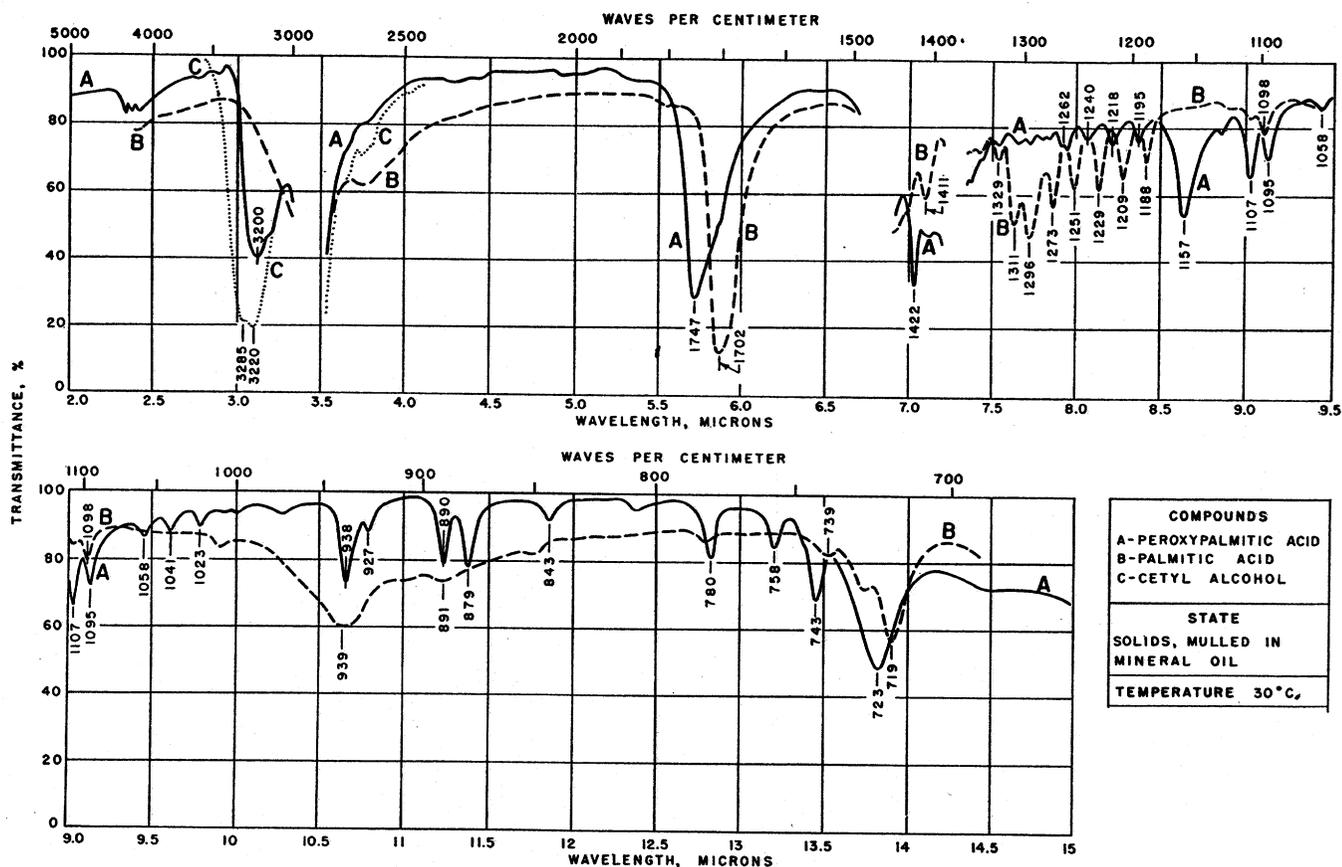


Figure 2. Infrared spectra of peroxy palmitic and palmitic acids and cetyl alcohol in solid state as Nujol mulls

hydroxyl band, the carbonyl frequency thus also suggests that the hydrogen bonding is less strong in the peroxy acid chelate than in the carboxylic acid dimer. The failure of peroxy acids to produce either an unbonded carbonyl (or hydroxyl) absorption band on high dilution, however, is a consequence of a favorable steric situation.

PEROXIDE REGION. Although skeletal

vibrations of the peroxide group (O—O) in various classes of organic peroxides have a wide frequency range [833 to 950 cm^{-1} (12 to 10.5 microns)], it is now fairly clear that many aliphatic peroxides absorb in the vicinity of the 850- to 890- cm^{-1} (11.5-micron) region. The peroxide group is a weak absorber in the infrared because the stretching mode of the O—O group is not

associated with any great change in dipole moment. Figure 3 shows the infrared spectral region in which the three classes of organic peroxides under discussion have their O—O absorption bands. For comparison, similar spectra are shown for the corresponding nonperoxidic analogs. Care must be exercised in interpreting bands found in the 850- to 950- cm^{-1} region, as both peroxides and other classes of organic compounds, such as oxiranes, may show important bands in this vicinity. A more detailed discussion of the infrared characteristics of organic peroxides is given in a recent paper (13).

Peroxy acids in solution (Figure 1, A, and Figure 3) show a broad band of medium intensity at about 865 cm^{-1} (11.56 microns), absent in the corresponding carboxylic acids. In the solid state, this band is difficult to assign in peroxy acids.

Relatively little work has been published on the infrared spectra and structures of aromatic peroxy acids. In 1951 Davison (2) studied peroxybenzoic acid and, on the basis of its spectrum and low melting point, concluded that it was normally monomeric in solution and that chelation was dimensionally possible. From Davison's study on a single aromatic peroxy acid, however, it can be tentatively concluded that

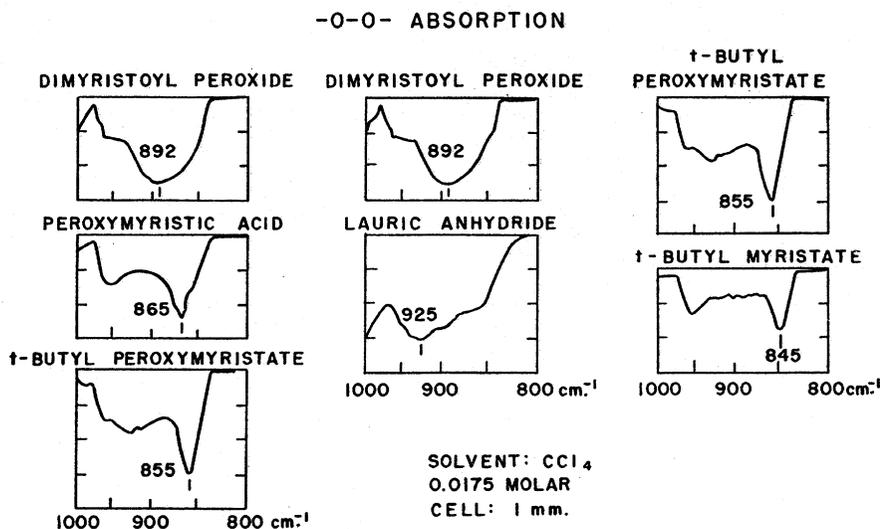


Figure 3. Peroxide absorptions of a diacyl peroxide, peroxy acid, and *tert*-butyl peroxy ester in infrared and comparison with nonperoxidic analogs

aromatic peroxy acids are structurally similar to the aliphatics.

X-Ray Diffraction Studies. The tentative conclusion mentioned earlier from infrared evidence, that aliphatic peroxy acids exist in the solid state as intermolecularly hydrogen-bonded dimers, is fully confirmed by long spacings determined by x-ray diffraction (17). The long spacing values increase regularly as the hydrocarbon chain increases. The average increase for each additional carbon atom is approximately 2.13 Å., a value considerably greater than the expected projected distance, 1.27 Å., of one C—C bond. It appears that the long spacing measured on the diffraction photographs are the projections of double the molecular length on $[d\ 001]$. Thus, the peroxy acid molecules, like the *n*-aliphatic acids and alcohols, must crystallize in bimolecular layers. The increase in long spacing for each additional carbon atom is $2.13/2 = 1.07$ Å., a value lower than the anticipated one of 1.27 Å. Peroxy acid dimers, therefore, are tilted with respect to the 001 plane.

In the earlier study published in 1955 (17), it was concluded that a single straight line is obtained by plotting long spacings against number of carbon atoms for even- and odd-numbered peroxy acids. This unexpected result suggested that the end packing of the peroxy acids was the same, and this conclusion appeared to be confirmed when a plot of melting points of peroxy acids against carbon number gave a single continuous curve. Repreparation of the peroxy acids and careful repetition and replotting of the x-ray diffraction and melting point results now suggest that the even and odd peroxy acids lie on separate curves, one for the odd and the other for the even carbon number peroxy acids (14).

Plots of long spacings (L.S.) against carbon number (*n*) form two almost parallel and nearly coincident straight lines, equations of which follow (14):

$$\text{L.S.} = 2.126n + 3.39 \text{ (5 odd peroxy acids)}$$

$$\text{L.S.} = 2.135n + 3.30 \text{ (6 even peroxy acids)}$$

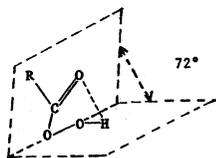
The difference between the lines is only about 0.08 Å., a small difference which appears to be real. The curves of melting points against carbon number are also close together, but the small difference between the odd and even numbers seems to be real and reproducible. Single-crystal studies now being conducted (5) are expected to resolve this problem.

Dipole Moment Studies. It was hoped that a comparison of the peroxy acid dimer lengths, calculated from known bond distances and angles obtained from a few possible models, with the measured long spacings just discussed would lead to a direct

establishment of their structure. This was not possible because the molecules are tilted, and the packing at the chain ends and the puckering, if any, of the five-membered chelate ring are not known. (The single-crystal studies referred to earlier should answer the question unequivocally, if adequate, stable single crystals can be grown.)

Early investigators in the peroxide field either assumed or stated that organic peroxides had a planar configuration (6, 18), even though it had been known for many years that hydrogen peroxide had a dihedral angle first reported to be 95° (9) but now believed to be about 120° in the free molecule (1, 10). One convenient technique for evaluating the extent of skew or puckering in organic peroxides is dipole moment studies. Thus, in 1952 Rogers and Campbell (12) using this technique, reported the dihedral angle in di-*tert*-butyl peroxide to be 123° and that in *tert*-butyl *n*-butyl peroxide to be 105° . In 1958, Miller and colleagues (7) of the University of Pennsylvania, under contract with our laboratory, studied the dipole moments of diacyl peroxides and reported a dihedral angle of about 100° .

In the same year, it was reported (11) that five (C_9 – C_{16}) aliphatic peroxy acids in benzene solution had the same dipole moment, $2.32 \pm 0.04D$, within experimental error. A reasonable model for the structure of the peroxy acids is:



In this model the $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O—O—}$ links are coplanar, as expected, from the double bond character of the bond joining the carbonyl carbon atom to the peroxy oxygen atom, and confirmed by earlier work on diacyl peroxides (?). The O—H link is bent out of the plane by an angle of $72^\circ \pm 4^\circ$ and represents a reasonable result of the effect of the hydrogen bonding on the barriers to rotation ordinarily present in peroxides.

Giguère and Olmos (4) assumed a planar structure for peroxy acids and proposed bond distances and angles in conformity with this concept. For their planar model the dipole moment observed should have been $1.83D$, nearly $0.5D$ less than the actual value. No reasonable changes in the bond moments for the O—H and C=O links in bond angles will bring the moment of the planar model close to $2.32D$. The planar structure for peroxy acids is completely untenable.

Molecular Weight and Miscellaneous Studies. Finally, if peroxy acids exist exclusively as chelated monomers in solution, their molecular weights and acid strengths should reflect this condition.

The molecular weights of peroxy acids remain constant in solution regardless of concentration (within the "ideal" solution range of 0.1 to 0.5 weight %) and the values are precisely those of the monomers (11, 17). In the same concentration range, carboxylic acids exist largely (70 to 90%) as dimers.

A further consequence of the proposed intramolecular hydrogen-bonded structure of peroxy acids is that they should be considerably weaker acids than the corresponding carboxylic acids. Studies with short-chain peroxy acids in essentially aqueous systems (3, 19) and with long-chain members in alcoholic systems (17) have shown that peroxy acids are approximately $1/1000$ as strong as the corresponding carboxylic acids.

DIACYL PEROXIDES AND *tert*-BUTYL PEROXYESTERS

Considerably less work has been published on the structure of diacyl peroxides and *tert*-butyl peroxy esters than on peroxy acids; the bulk of this work has been reported from our laboratory (15). Results are still inconclusive, but single-crystal studies now in progress should resolve the remaining structural problems.

X-ray powder data (15) were obtained on diacyl peroxides and *tert*-butyl peroxy esters and on analogous nonperoxide compounds—that is, anhydrides and *tert*-butyl esters, respectively. Crystallization in identical packing habits by analogous pairs of peroxide and nonperoxide compounds should permit a determination of some of the structural features associated with the peroxide linkage. The comparative method depends upon the existence of both a linear and parallel relationship for plots of long spacings against carbon atoms for the analogs.

Diacyl Peroxides. Extrapolation of the long spacing plots to zero carbon content for diacyl peroxides and anhydrides leaves an intercept value which represents all linear or chain-linked noncarbon atoms plus the long spacing contribution of each terminal hydrogen in the hydrocarbon link. [This intercept value must be divided by the sine of the angle (sine β) at which the compounds crystallize to the basal plane to obtain a corrected intercept value which represents its actual contribution to chain length.] The difference between the intercept values of the diacyl peroxides and anhydrides measures the contribution of the additional oxygen atom to the chain length (15).

Table I. Half-Wave Potentials and Diffusion Current Constants

tert-Butyl peroxy esters			Diacyl peroxides		
	$-E_{1/2}$	i_d/c		$-E_{1/2}$	i_d/c
C ₉	0.96	10.7	C ₁₈	0.10	9.1
C ₁₀	0.90	10.9	C ₂₀	0.10	10.0
C ₁₂	0.87	10.0	C ₂₄	0.09	9.6
C ₁₄	0.82	10.5	C ₂₈	0.12	8.2
			C ₃₂	0.10	7.7
			C ₃₆	0.08	6.2

The long spacings of the even diacyl peroxides are 0.4 Å. larger than those of the even anhydrides and the peroxides are a little less tilted. If even diacyl peroxides have the same end packing as the even anhydrides, a projected O—O group distance of 1.44 Å. is derived. If a normal hydrocarbon zigzag configuration were applicable to the peroxide group also, the calculated projected distance for the peroxide oxygens would be 2.10 Å., or 0.66 Å. larger than the experimentally derived value. The observed peroxide foreshortening of 0.66 Å. can be interpreted as evidence of a skewed O—O bond linkage rather than a chain-extended linkage. The O—O bond skew has the effect of telescoping two atoms to give the peroxide a superficial physical resemblance to the corresponding anhydride.

The skewing effect deduced from x-ray diffraction data had previously been demonstrated by dipole moment studies on diacyl peroxides by Miller and coworkers (?). The dipole moments, which are lower than those of the analogous anhydrides, were used by them to construct a structure with a dihedral angle of 100° between the C—O—O planes, coplanar in each C—C—O grouping and with both carbonyl groups oriented inward toward the O—O group.

The foreshortening of 0.66 Å. calculated from the x-ray data corresponds to a dihedral angle of 123° which, in view of the assumptions involved, is in fair agreement with the value of 100° derived from the dipole moment study (?).

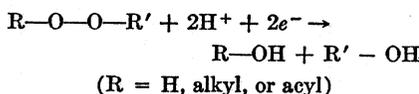
Alternation of long spacings is observed between even and odd diacyl peroxides, with the odd carbon members having slightly larger long spacings (15). The angles of tilt of both series appear to be nearly identical. Since only two odd carbon member diacyl peroxides were available for study, no attempts have been made to draw any conclusions about them.

tert-Butyl Peroxy Esters. tert-Butyl peroxy esters and the corresponding tert-butyl esters crystallize in highly tilted layers, as evidenced by the small change in long spacing per carbon atom, less than 1 Å. per methylene.

Furthermore, the long spacings of the tert-butyl esters are larger than those of the peroxy esters, which is the reverse of the relationship between diacyl peroxides and anhydrides. The comparative method is ineffective here and elucidation of the structure of tert-butyl peroxy esters will require single-crystal studies. Dipole moment studies suggest that the peroxy group is skewed (13).

POLAROGRAPHIC BEHAVIOR

Polarography is a versatile electro-metric method and is one of the best techniques for elucidation of peroxide structure and analysis when pure model compounds are available. The reductions are two-electron transfers leading to rupture of the O—O bond to form hydroxyl groups:



The half-wave potentials, $E_{1/2}$, depend on peroxide structure and relate to the bond strength of the group being reduced. The more negative the half-wave potential, the more difficult is the reduction. For example, di-tert-butyl peroxide, a very stable organic peroxide, is not reduced over the normal polarographic range using a benzene-methanol system and lithium chloride as the supporting electrolyte. For an aliphatic peroxide series having saturated alkyl chains exceeding two carbon atoms, the order of decreasing bond strength based on $E_{1/2}$ is:

Di-tert-butyl peroxide	>dialkyl peroxides	>tert-butyl peroxy esters	>hydroperoxides	>diacyl peroxides	>peroxy acids
$-E_{1/2}$, volts vs. S.C.E.	>2	>1	0.8-1.0	0.1	~0.05
E_A	38-40	36-37	35-36	30	24

The order of decreasing O—O bond strength determined polarographically parallels the decrease in activation energy E_A for thermal decomposition of these peroxides and their reactivity

with iodide ion (13). Of the three classes of organic peroxides with which we are concerned in this paper, polarography is a convenient tool for their determination and analysis and, in particular, for study of their reactions in solution if the medium is amenable to handling in a polarograph.

Table I shows the half-wave potentials and the diffusion current constants, i_d/c , obtained in our laboratory on tert-butyl peroxy esters and diacyl peroxides in benzene-methanol (1 to 1) solution with lithium chloride as the supporting electrolyte.

The peroxy esters ($E_{1/2} = -0.82$ to -0.96) reduce with nearly the same ease as hydroperoxides ($E_{1/2} = -0.6$ to -0.9) but are more difficult to reduce than peroxy acids ($E_{1/2} = -0.05$). Also, the half-wave potentials of the peroxy esters decrease with molecular weight increase, but the diffusion current constant, useful for quantitative determination, changes very little.

In contrast to the peroxy esters, the half-wave potentials of diacyl peroxides remain constant ($E_{1/2} = -0.08$ to -0.12) with increasing molecular weight but the diffusion current constants show a marked decline. A recent paper (17) from our laboratory discusses the relationship between diffusion current constants and molecular weights, but additional work is required to obtain a final answer.

Table II summarizes some of the structural and spectral data described in this paper.

LITERATURE CITED

- (1) Amako, Y., Giguère, P. A., *Can. J. Chem.* **40**, 765 (1962).
- (2) Davison, W. H. T., *J. Chem. Soc.* 1951, 2456.

Table II. Dihedral Angles and Infrared Absorption of Peroxides*

	Dihedral angle, °	O—O, cm. ⁻¹	C=O, cm. ⁻¹	OH and OOH, ^a cm. ⁻¹
H ₂ O ₂	120	877		3560
Peroxy acid	72	865	1748	6850, 4830, 3530, 3280, 947
tert-Butyl peroxy esters	100-165	855	1770	
Diacyl peroxides	~100	892	Doublet { 1775 (longer) 1803	

* Only important absorptions listed.

- (3) Everett, A. J., Minkoff, G. J., *Trans. Faraday Soc.* **49**, 410 (1953).
- (4) Giguère, P. A., Olmos, A. W., *Can. J. Chem.* **30**, 821 (1952).
- (5) Jeffrey, G., University of Pittsburgh, Pittsburgh, Pa., unpublished data.
- (6) Kasatochkin, V., Perlina, S., Ablesova, K., *Compt. Rend. Acad. Sci. URSS* **47**, 36 (1945).
- (7) Lobunetz, W., Rittenhouse, J. R., Miller, J. G., *J. Am. Chem. Soc.* **80**, 3505 (1958).
- (8) Parker, W. E., Ricciuti, C., Ogg, C. L., Swern, D., *Ibid.*, **77**, 4037 (1955).
- (9) Penney, W. G., Sutherland, G. B. B. M., *Trans. Faraday Soc.* **30**, 898 (1934); *J. Chem. Phys.* **2**, 492 (1934).
- (10) Redington, R. L., Olson, W. B., Cross, P. C., *Ibid.*, **36**, 1311 (1962).
- (11) Rittenhouse, J. R., Lobunetz, W., Swern, D., Miller, J. G., *J. Am. Chem. Soc.* **80**, 4850 (1958).
- (12) Rogers, M. T., Campbell, T. W., *Ibid.*, **74**, 4742 (1952).
- (13) Silbert, L. S., *J. Am. Oil Chemists' Soc.* **39**, 480 (1962).
- (14) Silbert, L. S., Lutz, D., Siegel, E., unpublished data from this laboratory.
- (15) Silbert, L. S., Witnauer, L. P., Swern, D., Ricciuti, C., *J. Am. Chem. Soc.* **81**, 3244 (1959).
- (16) Swern, D., *Chem. Revs.* **45**, 1 (1949).
- (17) Swern, D., Witnauer, L. P., Eddy, C. R., Parker, W. E., *J. Am. Chem. Soc.* **77**, 5537 (1955).
- (18) Walsh, A. D., *J. Chem. Soc.* **1948**, 331.
- (19) Wolf, R., *Bull. Soc. Chim. France* **1954**, 644.

RECEIVED for review December 7, 1962.
 Accepted February 19, 1963. Symposium on Organic Peroxides, Division of Analytical Chemistry, 142nd Meeting, ACS, Atlantic City, N. J., September 1962. The Eastern Regional Research Laboratory is a Laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Services, U. S. Department of Agriculture.