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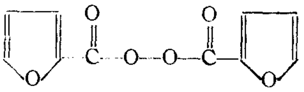
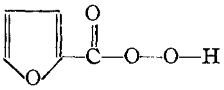
Studies in Organic Peroxides. III. Peroxides in the Furan Series

BY NICHOLAS A. MILAS AND AMBROSE MCALEVY

In a recent article[1a] the authors reported the synthesis of some peroxides and peracids structurally related to camphoric acid. The present communication describes some peroxides and peracids in the furan series. Difuroyl peroxide (I),[2] furoperacid (II) and difuryl acryloyl peroxide (III) have been synthesized and their properties studied.


I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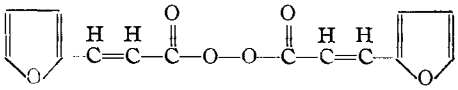
III

It has been found that these peroxides are far more unstable and consequently far more reactive than the corresponding peroxides of the benzene or camphoric acid series. Some of them, when dry, decompose spontaneously at room temperature and occasionally with explosive violence. Furoperacid has been synthesized as well as isolated as an intermediate product from the auto-oxidation of furfural.

Experimental

Difuroyl Peroxide.—To 200 cc. of ice water is added slowly with rapid stirring 17 g. of pure sodium peroxide; the temperature of the mixture at this and at subsequent stages of the reaction should not exceed +3°. Into this mixture is now dropped slowly, during forty-five minutes and under vigorous stirring, 50 g. of furoyl chloride (Eastman Kodak Company). Stirring is continued for one hour longer, then the solid peroxide separated by filtration, pressed on porous plate and allowed to dry in air at room temperature; yield of the crude product, 40.8 g. or 96% of the theoretical. This product is 97–98% pure, and to purify it further, it is dissolved in ether and shaken with a saturated solution of sodium carbonate. The ether solution is then dried over anhydrous sodium sulfate, the ether removed at room temperature under reduced pressure, and the peroxide dried in a vacuum desiccator over concentrated sulfuric acid. The pure peroxide forms in light yellowish needles melting at 86–87° (dec.).

Anal. Calcd. for $C_{10}H_6O_6$: active (O), 7.21. Found: active (O), 7.3, 7.29, 7.24.

Difuroyl peroxide is stable under ordinary conditions but explodes violently on heating or rubbing. Its solubility in ether at 25° is 6.4 g. per 100 cc. of ether. It is also soluble in acetone, methanol, chloroform, carbon tetrachloride and benzene; insoluble in water or petroleum ether.

Difurylacryloyl Peroxide.—This peroxide was synthesized from sodium peroxide and furylacryloyl chloride. We made both the acid chloride[3] and the acid[4] from which it was prepared, and their properties agreed very well with those described in the literature.

To 50 g. of finely broken ice is slowly added with vigorous stirring 1.3 g. of pure sodium peroxide, and into this mixture is dropped, during fifteen minutes, a solution of 50 cc. of anhydrous ether containing 6 g. of furylacryloyl chloride. At no time during the reaction should the temperature be allowed to rise above 0°. After the last addition of the acid chloride, the mixture is stirred for one hour longer, then extracted with 100 cc. of a 1–1 mixture of ethyl ether and ethyl acetate. The extract is then washed several times with a saturated solution of sodium carbonate, and dried over anhydrous sodium sulfate. When the solvent is removed under reduced pressure, the peroxide separates out into white, crystalline needles which melt at 104° (with dec.); yield, 1.2 g.

Anal. Calcd. for $C_{14}H_{10}O_6$: C, 61.31; H, 3.65; active (O), 5.83. Found: C, 61.27; H, 3.56; active (O), 6.06, 5.80, 5.65.

The pure peroxide is white but becomes yellowish in a very short time on standing at room temperature. This can be recrystallized easily from a 1–1 mixture of ether and ethyl acetate. It is soluble in acetone and ethyl acetate; slightly soluble in ether. On heating, it explodes violently.

Furoperacid.—To a solution of 300 cc. of anhydrous ether containing 10 g. of difuroyl peroxide and cooled in an ice–salt mixture to −5° is added slowly with vigorous shaking 40 cc. of ice-cold, acetone-free methyl alcohol containing sodium methylate equivalent to 1.1 g. of sodium. The mixture is then poured on 100 cc. of ice water, the non-aqueous layer removed, and the aqueous layer first extracted with 100 cc. of cold chloroform, then mixed with 100 cc. more of the latter. The mixture is now acidified at 0° with cold 6 *N* sulfuric acid, and the chloroform, which contains most of the peracid, is removed and the aqueous layer extracted twice with 50 cc. of chloroform. The chloroform solution is finally dried over anhydrous sodium sulfate and the chloroform removed at room temperature under reduced pressure; yield of the crude product having a purity of 86%, 4.9 g. or 87.8% of the theoretical. This product is recrystallized from carbon tetrachloride at −5° to colorless needles melting at 59.5° (dec.).

Anal. Calcd. for $C_5H_4O_4$: active (O), 12.49. Found: active (O), 12.2, 12.2, 12.35.

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[1] (a) Milas and McAlevy, THIS JOURNAL, **55**, 349 (1933); (b) Milas and Cliff, *ibid.*, **55**, 352 (1933).

[2] *Cf.* Gelissen and van Roon, *Rec. Trav. Chim.*, **43**, 359 (1924).

[3] Gilman and Wright, *Iowa J. Sci.*, **3**, 109 (1929).

[4] Gibson and Kahnweiler, *Am. Chem. J.*, **2**, 314 (1890).

Furoperacid is very soluble in water, and on standing in this solvent hydrolyzes to furoic acid and hydrogen peroxide. It is soluble in nearly all common organic solvents except petroleum ether, in which it is insoluble. The solid peracid is fairly stable at 0°, but decomposes rapidly at 30–40° with the evolution of oxygen and carbon dioxide. Its stability under various conditions will be discussed in a subsequent article. In chloroform solution the peracid is perfectly stable at 0° for long periods of time, and consequently it can be used for the estimation of unsaturation of various organic substances. In most cases, the estimation of unsaturation can be followed quantitatively with the technique used in a previous article of this series.[1b] The results obtained with some unsaturated organic substances are recorded in Table I. Each sample was allowed to stand at room temperature with the chloroform solution of the peracid for about one hour before titration. It may be seen from this table that some of the unsaturated substances fail to give quantitative results with furoperacid, a behavior which is encountered with other peracids.

TABLE I

FUROPERACID AND UNSATURATION

Substance	No. of double bonds	Moles of peracid[a] consumed
Iso-eugenol	1	1.037
Iso-safrole	1	1.081
Safrole	1	1.015
Cholesterol	1	1.020
Ergosterol	3	3.127
Citronellol	1	1.043
Pinene	1	1.083
Limonene	2	1.685
Geraniol	2	1.380
Tetramethylethylene	1	0.29
Allyl alcohol	1	.15
Furoic acid	1	.00

[a] Average of at least two determinations.

Furoperacid from the Auto-oxidation of Furfural.—Furfuraldehyde, like benzaldehyde, absorbs a molecule of oxygen to form an intermediate peroxide which probably goes over to the more stable furoperacid, but it has not been possible up to the present time to detect, even qualitatively, any substance of peroxidic nature in the auto-oxidation products of furfural. It appears, therefore, that the peroxide formed in this reaction is much too unstable and reactive and either decomposes spontaneously or oxidizes the furfural faster than it undergoes rearrangement to the more stable furoperacid. We had already discovered that ultraviolet light had an accelerating effect not only on the auto-oxidation of furfural, but also on the decomposition of the synthetic furoperacid, so we decided to determine experimentally whether the initial peroxide formed in the auto-oxidation of furfural was a peracid of the same properties as our synthetic product.

After some trials with different quantities of furoperacid in furfural, the irradiation of a solution of 0.0085 g. of the peracid in 5 cc. (5.8 g.) of furfural[5] contained in a quartz flask under pure nitrogen, with a quartz mercury lamp provided with a Corning plate filter G586 AW, gave the most satisfactory results. At the end of one hour of irradiation at 25° and at a distance of 30.4 cm. from the filter plate, the peracid had not been completely used up, as determined by the liberation of iodine.

In another experiment, using exactly the same conditions except that the peracid was left out, 5 cc. of pure furfural was allowed to oxidize in the presence of air with the quartz flask constantly shaken to ensure a sufficient supply of oxygen. The oxygen absorbed was measured accurately, under atmospheric pressure, in a calibrated semi-microburet which was attached to the system. In order to remove any carbon dioxide that might have formed during the reaction, a glass tube containing ascarite was connected between the microburet and the quartz flask. Following a seventy-five minute period of comparatively slow oxygen absorption, the total oxygen absorbed during the subsequent hour amounted to 3.24 cc., which is sufficient to form 0.0185 g. of peracid. The resulting mixture, however, contained no product of peroxidic nature, indicating that the initial peroxide formed in the auto-oxidation of furfural disappeared at a rate more than twice that of the synthetic peracid in the previous experiment. Furthermore, this experiment shows that the rate of disappearance of the initial peroxide is greater than the rate of its formation. One may conclude, therefore, that the initial peroxide formed in the auto-oxidation of furfural is different from the synthetic peracid, although it may rearrange under favorable conditions to give this peracid. We are of the opinion that the initial peroxide is probably a moloxide of the type advocated elsewhere by one of us.[6]

The synthetic furoperacid, in chloroform and in the presence of furfural, does not disappear rapidly at 0°. For example, after forty hours of standing at this temperature, a chloroform solution of furfural containing a large excess of the peracid lost only 20.9% of its activity equivalent to 0.901 mole of the peracid per mole of furfural. It was also found that furoperacid is sparingly soluble in low boiling petroleum ether, so it was decided to perform the auto-oxidation of furfural in this solvent at 0°, with the hope of isolating the stable furoperacid. Accordingly, a solution of 7.5 g. of freshly distilled furfural in 500 cc. of petroleum ether (b. p. 36–58°, and free from unsaturated hydrocarbons), contained in a large quartz flask, was allowed to auto-oxidize at 0° and under the influence of ultraviolet light which was filtered as before and placed at a distance of 30.4 cm. from the quartz flask. After two and one-half hours of irradiation, the solution gave a strong peroxide reaction. The auto-oxidation was then discontinued and the solution cooled to −15°, thereby separating into two distinct layers, with the lower layer containing practically all of the peroxide mixed with unconverted furfural, furoic acid and other products. This layer was separated and treated with a 10% solution of potassium hydroxide mixed with broken ice, and the mixture extracted several times with cold ethyl ether to remove the products that failed to dissolve in the alkali. Finally, the alkali solution was acidified with cold dilute sulfuric acid, again extracted with ether, and the latter separated and dried over anhydrous sodium sulfate.

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(5) The furfural used in these experiments was freshly distilled under reduced pressure from the commercial product kindly furnished by the Quaker Oats Company.

(6) Milas, *Chem. Rev.*, **10**, 295 (1932); *J. Phys. Chem.*, in press.

When the ether was removed, under reduced pressure, a white solid separated which reacted with potassium iodide as though it contained a peracid. Our attempts to separate the peracid in the pure form from this solid were not successful. However, the results are convincing in showing that, under the conditions of our experiment, a fairly stable peracid is obtained in small quantities from the auto-oxidation of furfural, and that this peracid may be identical with the synthetic furoperacid.

Summary

1. Difuroyl peroxide, furoperacid and difurylacryloyl peroxide have been synthesized and their properties recorded.

2. It has been shown that furoperacid can be used, in many cases, for the quantitative estimation of unsaturation.

3. A peracid, which is believed to be identified with the synthetic furoperacid, has been isolated from the auto-oxidation of furfural.

4. It has been found, however, that the initial peroxide formed during the auto-oxidation of furfural is far more unstable and reactive than the synthetic furoperacid, and therefore is not identical with the latter, although, under favorable conditions, it can rearrange to give the furoperacid.

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Studies in Organic Peroxides. IV. The Spontaneous Decomposition of Furoperacid

BY NICHOLAS A. MILAS AND AMBROSE MCALEVY

A careful study of the spontaneous decomposition of organic peracids, under various conditions, may yield some valuable information with regard to the role which they play as intermediate products in the auto-oxidation of aldehydes or other organic substances. The present investigation deals with the spontaneous decomposition of furoperacid[1] in the solid state as well as in solution.

Spontaneous Decomposition of Solid Furoperacid.—The rate of the spontaneous decomposition of furoperacid is influenced by the temperature and the presence of certain types of solids. The decomposition appears to behave like a reaction in the solid phase commencing at certain "active spots" or "nuclei" which are probably formed on the corners or edges of crystals.[2] That reaction commences at certain spots is easily shown by the fact that, on standing at room temperature, the crystalline furoperacid develops brownish spots which are scattered throughout the crystalline mass. Furthermore, when the crystals, taken from different parts of the preparation, are analyzed for active oxygen, the values obtained differ slightly from one another, showing that the crystalline peracid does not decompose uniformly but in spots. In determining the stability of the solid peracid at 0°, we came up against this difficulty, so that the results given in column 2 of Table I are really averages of two or more determinations taken from different parts of the crystalline solid.

TABLE I

THE SPONTANEOUS DECOMPOSITION OF SOLID FUROPERACID

Time, hrs.	0	24	72	96	122	145	170	204
% active (O)	10.25	10.32	10.20	9.80	9.29	9.61	9.07	8.81

From this table it may be seen that the spontaneous decomposition of the solid peracid at 0° exhibits an induction period of seventy-two hours. This induction period is shortened with increase of temperature until at 40° the reaction becomes so violent within a short time that it detonates.

That the rate of the spontaneous decomposition of solid furoperacid is influenced by the presence of other solids is clearly seen by the results recorded in Table II. It was originally found that, when large crystals of the various solids were used with the peracid, the time elapsed (induction period) between mixing and the occurrence of the explosion could not be easily reproduced, so it was necessary to powder well, just before mixing both the peracid and each one of the solids. The mixing was done rapidly in a 8-cm. test tube fitted with a cork stopper and shaken to ensure

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(1) Milas and McAlevy, THIS JOURNAL, **56**, 1219 (1934).

(2) *Cf.* The thermal decomposition of barium azide, mercuric fulminate, and other explosive substances. Garner and co-workers. *Proc. Roy. Soc.* (London), **139A**, 576 (1933); *J. Chem. Soc.*, 1393, 1398 (1933).