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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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 110]

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).

thorough mixing. The quantities usually used were 0.1 g. of the peracid to 0.1 g. of the solid. All solid substances used were of the highest purity obtainable. In some cases the explosions were instantaneous while in others the induction period ranged from one-half to ten minutes. All explosions were accompanied by the evolution of light and of considerable gas having a pungent odor. A brown tarry residue was also formed at the same time.

TABLE II

THE EFFECT OF DIFFERENT SOLID SUBSTANCES ON THE SPONTANEOUS DECOMPOSITION OF FUROPERACID

Substance	Induction period, min.	Remarks
Inorganic		
Sodium fluoride	No effect	
Sodium chloride	No effect	
Sodium bromide	0.5	Moderate explosion
Sodium iodide	.5	Moderate explosion; I_2 evolved
Potassium fluoride	1.0	Violent explosion; no Cl, Br or I present
Potassium chloride	2.5	Violent explosion
Potassium bromide	Instant.	Moderate explosion
Potassium iodide	3.0	Moderate explosion; I_2 evolved
Rubidium chloride	1.0	Violent explosion; reddish flame of about 2 ft. long
Cesium chloride	Instant.	Violent explosion
Magnesium chloride (hydrated)	6.5	Violent explosion
Calcium chloride (anhydrous)	Instant.	Violent explosion
Barium chloride (hydrated)	3.0	Violent explosion
Strontium chloride	0.5	Violent explosion
Sodium hydrogen sulfite	2.0	Violent explosion
Sodium thiosulfate	Instant.	Moderate explosion
Potassium sulfite (hydrated)	10.0	Moderate explosion
Potassium sulfate	No effect	
Potassium hydroxide	Instant.	Moderate explosion
Potassium bromate	No effect	
Thorium oxide (powder)	No effect	
Metals		
Platinum foil	No effect	
Electrolytic silver	No effect	
Iron filings	No effect	
Organic		
Ergosterol	1.0	Moderate explosion
Pyrogallol	1.0	Moderate explosion
Animal charcoal	1.5	Violent explosion; no Cl, Br or 1 present
Sugar charcoal (powder)	No effect	

The results recorded in Table II seem to indicate that the effect of various solids on the decomposition of the solid peracid is not one of surface, but presumably one in which a local reaction causes a local evolution of heat energy which accumulates in the active spots through a chain process, and which subsequently acts as a "trigger" to set off the peracid. It may be stated, however, that the local reaction is not one of oxidation in every case. Potassium hydroxide is not oxidized by the peracid, yet its effect is instantaneous. Furthermore, one would certainly not expect the peracid to oxidize potassium fluoride, which resists oxidation even by the strongest oxidizing agents. The effect of potassium fluoride is probably due to the formation of an addition complex with the peracid, since Tanatar[3] has already shown that this salt forms a fairly stable complex with hydrogen peroxide.

The induction period and the violence of explosion, in the cases in which local oxidation of the solid is assumed to be the reaction leading to explosion, do not seem to be related with the ease of oxidation of the solid in question. In the case of potassium iodide, for example, in which the oxidation is evident by the evolution of iodine, the explosion is moderate and the induction period much longer than with potassium chloride.

To determine the extent of oxidation with potassium chloride, three samples were allowed to explode in such a way as to prevent any loss of the solid material. The furoic acid was then extracted from each sample with chloroform (free from mineral acid), and the residue in each sample dissolved in 100 cc. of distilled water. The alkalinity of each sample was then determined according to the Hehner method by adding 5 cc. of chloroform and 2 cc. of 0.05% erythrosine.[4] This method allows the determination of small amounts of alkali in presence of small amounts of weak organic acids. A blank was run with the potassium chloride alone, and it was found that there was no detectable difference in the alkalinity of the blank and that of the actual samples. Since the accuracy of our titrations was limited by the sensitiveness of our indicator (0.05 cc. of 0.035 N sulfuric acid), the amount of alkali formed by the explosion in each case must have been less than 0.05×0.00228 g. or about 0.1 mg.

Ultraviolet light in the region of 4500 to 3600 Å. also accelerates the decomposition of solid furoperacid. Powdered furoperacid in a quartz test-tube was exposed to screened ultraviolet (Corning filter G 586 AW) at a distance of 5 cm. from the screen and at a temperature of 26°. At the end of twenty minutes of exposure, the furoperacid decomposed suddenly and completely, without

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[3] Tanatar, *Z. anorg. Chem.*, **28**, 255 (1901).

[4] Ellms, THIS JOURNAL, **21**, 359 (1899).

detonation, into a brownish gummy mass. This experiment clearly indicates that energy alone in the form of ultraviolet radiation can accelerate the decomposition of solid furoperacid.

To find whether the extent of surface plays an important part in the effect described in the foregoing pages, different amounts of well-powdered solid potassium chloride were mixed with the same amount of the peracid and the induction period again determined. The results are shown in Table III.

TABLE III

EFFECT OF POTASSIUM CHLORIDE ON THE SPONTANEOUS DECOMPOSITION OF SOLID FUROPERACID

Per-acid, g.	Potassium chloride, g.	Induction period, min.
0.1	0.1	2.5
.1	.01	3.0
.1	.005	3.5
.1	.001	No explosion, but reaction on standing overnight

These results show that a minimum amount of potassium chloride can be reached which fails to cause the explosion [illegible] the peracid, although the minimum amount [illegible] this salt which causes acceleration of the decomposition without explosion has not been estimated. The results further indicate that surface has a definite effect, and the greater the surface, up to a certain limit, the greater the number of active spots which induce the explosion of furoperacid. It may be stated here that these results give us a clearer understanding of the role which potassium chloride plays in gaseous oxidation reactions in which the reaction vessels are coated with this salt.[5] A wider choice of salts can now be made which will have either greater or smaller effect than potassium chloride.

Analysis of the Decomposition Products of Solid Furoperacid.—Solid benzoperacid has been reported[6] to decompose into benzoic acid and oxygen. It was therefore surprising to find that the gaseous products resulting at 35° from the decomposition of solid furoperacid consist mainly of carbon dioxide. The analyses of the gases in three experiments are recorded in Table IV. In experiment 2 the decomposition was allowed to take place in an atmosphere of nitrogen, while in experiments 3 and 4 it took place in a vacuum (0.5 mm.).

TABLE IV

GASEOUS PRODUCTS FROM THE DECOMPOSITION OF FUROPERACID

Expt.	2	3	4
CO_2, %	81.7	100	100
O_2, %	18.3	0	0

The rate of gas evolution was determined accurately in the case of experiment 4 and was found to be auto-accelerated as shown in Table V.

TABLE V

RATE OF GAS EVOLUTION FROM THE DECOMPOSITION OF SOLID FUROPERACID

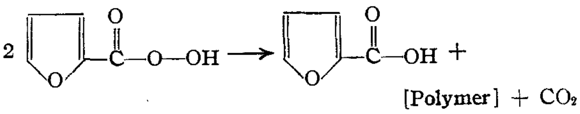
Time, hrs.	0.5	1.0	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Press. increase, mm.	2.0	6.5	17.0	27.0	34.0	41.0	44.5	46.0	46.0

The products of decomposition were separated out quantitatively in the case of experiment 3, and were found to consist of 10.1% of carbon dioxide, 50.7% of furoic acid, 37% of a yellowish, resinous, alkali-soluble polymer and 1.5% of 4,5-epoxyfuroic acid or 5-hydroxyfuroic acid. The last named substance was isolated in the form of its barium salt.

Anal. Calcd. for $C_{10}H_6O_8Ba \cdot 1.5H_2O$: C, 28.6; H, 2.15; Ba, 33.11; H_2O, 6.44. Found: C, 28.2; H, 2.8; Ba, 33.0; H_2O, 5.95.

This substance has no melting point, since it loses carbon dioxide very readily and long before it melts, yielding a black amorphous product. Such a behavior has also been found in the case of 5-hydroxyfuroic acid.[7] However, the initial product is, in our opinion, 4,5-epoxyfuroic acid which has a lactone structure analogous to that of lactone acids which are known to lose readily carbon dioxide.[8] That the addition of furoperacid fails to take place in the double bond next to the carboxyl group has been amply demonstrated elsewhere.[9] Hence, the addition actually took place first in the 4,5 position, resulting in the epoxyfuroic acid.

From the foregoing results, one may represent the spontaneous decomposition of the solid furoperacid at 35° by the equation



Since the amount of 4,5-epoxyfuroic acid formed is very small, its production is probably the result

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[5] Pease, THIS JOURNAL, **55**, 2753 (1933).

[6] Erlenmyer, *Helv. Chim. Acta*, **10**, 620 (1927).

[7] Cross, Bevan and Heiberg, *J. Chem. Soc.*, **75**, 749 (1899); Cross, Bevan and Briggs, *Ber.*, **33**, 3132 (1900).

[8] Darzens, *Compt. rend.*, **195**, 885 (1932).

[9] Milas and Cliff, THIS JOURNAL, **55**, 352 (1933).

of a side reaction between the furoperacid and furoic acid.

Spontaneous Decomposition of Furoperacid in Solution.—Furoperacid is more stable in solution than it is in the solid state. For example, a chloroform solution containing 50 millimoles of the peracid per liter shows no change even after 170 hours of standing at 0°. Even at 25°, the rate of decomposition is too slow to permit accurate measurements. The data shown in Tables VI and VII have been obtained at 35° and at 40°, respectively, each value representing a separate determination. To prevent evaporation of the solvent, samples of equal volume were accurately measured from a stock solution into a series of 20-cc. glass-stoppered bottles all of which were then placed in the thermostat at the same time. The first sample in each series was discarded, and after a definite period of time, each subsequent sample was withdrawn and titrated for active oxygen. From the results obtained and the initial concentration, which was 55.6 millimoles per liter in the first series and 54.1 millimoles per liter in the second series, the percentage decomposition was calculated; this is shown in column 2 of each table.

TABLE VI

DECOMPOSITION OF FUROPERACID IN CHLOROFORM AT 35°

Time, hrs.	Decomposition, %	k
10.8	6.5	0.0063
17.5	7.7	.0046
35.5	18.7	.0058
43.5	21.6	.0056
59.3	29.0	.0058
66.2	32.0	.0058
83.2	36.5	.0055
87.2	41.8	.0062
108.2	46.7	.0058
114.5	47.8	.0057
142.5	61.1	.0066
	Mean	.0058

TABLE VII

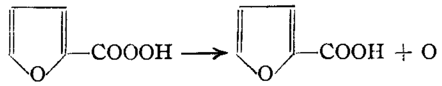
DECOMPOSITION OF FUROPERACID IN CHLOROFORM AT 40°

Time, hrs.	Decomposition, %	k
16.2	11.8	0.0078
23.5	18.7	.0087
40.5	29.7	.0088
47.5	34.5	.0089
65.8	43.7	.0088
71.8	46.9	.0088
96.5	57.1	.0090
136.5	72.5	.0095
	Mean	.0088

The average values for the monomolecular constants at 35 and at 40° are 0.0058 and 0.0088, respectively, and the temperature coefficient and the heat of activation calculated from these constants are 2.30 per 10° rise, and 15,800 calories per mole of the peracid, respectively. When these constants with the heat of activation are combined in the form of the Arrhenius equation, one derives the following equation which represents the decomposition of furoperacid in chloroform solution

$$k = 1.035 \times 10^{9} e^{-15,800/RT}$$

By analysis of the decomposition products, we found that the decomposition of furoperacid in chloroform solution gives mainly furoic acid, and can therefore be represented by the equation



But the decomposition of furoperacid also gives a small amount, about 3%, of a low melting point product having higher acidity and lower volatility than furoic acid. Apparently there is an unimportant very slow secondary reaction probably between the peracid and itself, or the peracid and furoic acid. In spite of this, however, the monomolecular nature of the main reaction does not seem to be affected. Results of similar nature have been reported by Hinshelwood and his co-workers[10] in discussing the monomolecularity of the decomposition of ozone in carbon tetrachloride solution. It is our future purpose to test the monomolecularity of the decomposition of other peracids which are known to decompose quantitatively to the corresponding acids.

The decomposition of furoperacid in solution is accelerated by ultraviolet light in the region of 4500 to 3600 Å. Glacial acetic acid was found to be the best solvent for this reaction, since both chloroform and carbon tetrachloride are affected by the ultraviolet light in the presence of our peracid. The solution, contained in a quartz flask, was exposed to screened ultraviolet light from a quartz mercury lamp at 25° and at a distance of 25 cm. from the screen. The results are shown in Table VIII.

TABLE VIII

EFFECT OF ULTRAVIOLET LIGHT ON THE DECOMPOSITION OF FUROPERACID IN GLACIAL ACETIC ACID SOLUTION

Time, hrs.	Peracid (U. V.), millimoles per liter	Peracid (dark), millimoles per liter
0	20.6	20.9
4	18.8	20.4
% decomposed	8.72	2.39

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[10] Bowen, Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.* (London), **134A**, 211 (1931).

Summary

1. It has been found that solid furoperacid decomposes spontaneously at 35°, yielding furoic acid, carbon dioxide, a resinous, alkali-soluble polymer and small amounts of 4,5-epoxyfuroic acid.

2. The decomposition of solid furoperacid is brought about, at room temperature, by certain types of inorganic and organic solids, and also by ultraviolet light in the region of 4500 to 3600 Å. An explanation has been offered to account for this effect.

3. It has also been found that furoperacid in chloroform solution decomposes mainly into furoic acid and oxygen.

4. The decomposition of furoperacid in chloroform has been measured at 35 and at 40°, and has been found to obey the monomolecular law. The temperature coefficient was found to be 2.30, and the heat of activation 15,800 calories per mole. The decomposition in chloroform can therefore be represented by the equation, $k = 1.035 \times 10^9 e^{-15,800/RT}$.

5. Ultraviolet light in the region of 4500 to 3600 Å. accelerates considerably the decomposition of furoperacid in glacial acetic acid solution.

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[CONTRIBUTION FROM THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

Transformation of the Methoxyl Group in Lignin in the Process of Decomposition of Organic Residues by Microörganisms[1]

BY SELMAN A. WAKSMAN AND H. W. SMITH

It has been established definitely[2] that the lignin constituents of plant residues play a highly important role in the process of humus formation. Because of the resistance of lignin to decomposition by the great majority of microörganisms, it is allowed to accumulate in soils, peats and composts; however, lignin does not remain in an unmodified form in the humus, but it undergoes certain changes, both of a purely chemical and biological nature. Comparatively little is known concerning the modifications of the lignin in the process of humus formation, largely because of the limited knowledge of the chemical structure of its molecule.

Among the characteristic groups of the lignin molecule, the methoxyl (OCH_3) has been studied most extensively, and has been found to play a prominent part in the transformation of the lignin into humus. This group is present in lignin both in ester and in ether combinations. The determination of the methoxyl content in the ether form is frequently taken as a measure of the lignin content of the plant material. Powell and Whittaker[3] concluded that the lignin molecule (flax lignin prepared by alkali extraction) contains four methoxyl groups and five hydroxyl groups capable of acetylation, only three of the latter being phenolic in character. According to Brauns and Hibbert,[4] spruce lignin contains five methoxyl groups and five free hydroxyl groups, three of which are aliphatic in character, one phenolic or enolic, and one reacting with alkylating reagents. The methoxyl content of lignin has been shown to vary in concentration in lignins of different plants,[5] and even in the lignin of the same plant, at different stages of growth;[6] it may also depend on the position of the lignin in the plant tissues, the methoxyl content of the lignin in the middle lamella of wood having been found[7] to be 11–13%, while that of the lignin in the cell wall was only 4.3–4.8%.

According to Beckmann, Liesche and Lehmann,[6] there is not only an increase in the lignin content of plants with an increase in maturity, but the amount of methoxyl in the lignin also increases. Fuchs[5] concluded that formation and methylation of lignin do not go hand in hand, and that methylation is a secondary process. Assuming that the methoxyl present in wood is due entirely to lignin, he calculated for "native lignin"

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[1] Journal Series Paper of the New Jersey Agricultural Experiment Station, Department of Soil Microbiology.

[2] S. A. Waksman, *Trans. Second Comm. Intern. Soc. Soil Sci. Budapest*, 3 (1929); *Cellulosechem.*, **11**, 209 (1930); J. Page, *J. Agr. Sci.*, **20**, 455 (1930).

[3] W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **125**, 357 (1923); **127**, 132 (1925).

[4] F. Brauns and H. Hibbert, THIS JOURNAL, **55**, 4720 (1933).

[5] W. Fuchs, "Die Chemie des Lignins," Verlag Julius Springer, Berlin, 1926.

[6] E. Beckmann, O. Liesche, and F. Lehmann, *Biochem. Z.*, **139**, 491 (1923).

[7] G. J. Ritter, *Ind. Eng. Chem.*, **17**, 1194 (1925); **18**, 608 (1926).