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Permonosulfuric Acid in Organic Media[*]

BY GERRIT TOENNIES

Permonosulfuric acid as an oxidizing agent in organic synthetical work has been employed almost exclusively in the form of aqueous solutions.[1] It is the purpose of this paper to record some data on the behavior of permonosulfuric acid in various alcohols and in a nitrile.

Permonosulfuric Acid, Preparation and Analytical.—The peracid was prepared either from potassium persulfate and sulfuric acid (method A)[2a] or from hydrogen peroxide[2b] and chlorosulfonic acid (method B).[3] Permonosulfuric acid was determined iodometrically by thiosulfate (about 0.025 *N*) titration. When the excess of iodide is kept small (about 0.005 *M*), the first end-point obtained on *rapid* titration, *immediately* after adding the peracid to a solution containing starch, potassium iodide and, if necessary (for securing an excess of acid over the iodide consumed), some sulfuric acid, corresponds to permonosulfuric acid (as established by comparison with the more generally specific method of Müller and Holder[4]). The accuracy of the initial reading can be improved by subtracting a correction equal to the small additional amount of iodine liberated on waiting again as long as was required to reach the first end-point. A subsequent end-point obtained after addition of molybdate yields the sum of permonosulfuric acid and hydrogen peroxide as long as persulfuric acid ($H_2S_2O_8$) is present in minor amounts. The total peroxygen was determined according to Lubarski and Dikowa.[5] Free acidity, including one acid group of H_2SO_5,[6] is obtained at the methyl red end-point, while five to ten minutes of boiling with excess (about 0.01 *N*) sodium hydroxide was found necessary[7] for the determination of total acidity ($H_2SO_5 \longrightarrow H_2SO_4 + O$, $H_2S_2O_8 + H_2O \longrightarrow 2H_2SO_4 + O$). In the concentrated peracid solutions prepared according to method B (*vide infra*) water was calculated by the difference between the sum of the directly determined constituents and the total.

Permonosulfuric Acid in Organic Media. General.—The relative stability of permonosulfuric acid solutions in 75% methanol has been mentioned.[8] Solutions containing about 10% water were made with 92% ethanol, and others of 3 to 5% water content, with isopropyl alcohol (98-99%, "petrohol"), isoamyl alcohol (Merck Reagent) and acetonitrile (Merck Reagent). Reaction mixtures obtained by method A[9] were stirred by portions into the solvent, which was kept below −15° by addition of solid carbon dioxide. In the case of isoamyl alcohol it was found preferable to grind the alcohol (of −15°) in portions into the almost solid reaction mass contained in a mortar imbedded in freezing mixture (thus dispensing with the need for carbon dioxide). In the cases of the lower alcohols or acetonitrile the insoluble salt is filtered by suction, while an amyl alcohol solution is better separated by centrifuging. Other solutions, of low H_2SO_4:H_2SO_5 ratios, were made by carefully adding concentrated peracid, prepared according to method B, to alcohol of less than −10° (*vide infra* on explosions).

Yields.—Table I gives a summary of the solutions prepared on the basis of method A. The fact (not shown in the table) that the total peroxygen recovery, *i. e.*, including the amount found in the solid residue, was 96–100% of that contained in the starting material, indicates that the yield of permonosulfuric acid in solution is limited by incompleteness of the reaction between sulfuric acid and persulfate and by incomplete separation from the solid residue (in order to maintain the concentration of the filtrate as high as possible no washings were added) rather than by loss of oxygen. Variations in the time the sulfuric acid–persulfate reaction mixture was allowed to stand (one to eighteen hours at 0° or two hours at room temperature) showed no definite effect on the yield. The solid residue appears to be chiefly $KHSO_4 + H_2O$ and additional H_2SO_4, approaching $2KHSO_4 + H_2SO_4$ in the case of isoamyl alcohol. In the ethanol experiment the washed and dried (at 125°) residue weighed 128 g. which, calculated as $KHSO_4 + H_2O$ (acid equivalent found 149, calculated 154), is equal to 98.5% of the potassium used. Three preparations according to method B, from 140, 160 and 250 mml. of chlorosulfonic acid and the equivalent amounts of hydrogen peroxide (85, 81 and 91%, respectively[2b]), gave permonosulfuric acid yields of 77 ± 1%. The resulting oily solutions (they did not crystallize at −15°) contained per gram, 6.2 ± 0.3 mml. of H_2SO_5, 1.9 ± 0.1 mml. of H_2SO_4, 0.8 ± 0.3 mml. of H_2O_2, 3.4 ± 0.6 mml. of H_2O, 0.0–0.2 mml. of $H_2S_2O_8$ and less than 0.02 mml. of Cl_2. These solutions keep well at low temperatures. At −12° the determined molarities of H_2SO_5 and H_2O_2 had changed from 6.01 and 0.80 to 6.19 and 0.65 after fourteen days and to 6.09 and 0.57 after fifty-nine days. However, care must be exercised in handling since contact with such organic matter as textiles, wood, paper causes immediate ignition.

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(1) *Cf.* Houben. "Methoden der organischen Chemie," Vol. 2, third ed., p. 222, 1925. The only exceptions were found in a paper published in 1900 by Baeyer and Villiger [*Ber.*, **33**, 860, 862 (1900)] who used dilutions of their "dry Caro reagent" in acetic acid and in ethanol.

(2) (a) Baeyer and Villiger, *ibid.*, **32**, 2628 (1899); Gleu, *Z. anorg. allgem. Chem.*, **195**, 70 (1931), and others; (b) obtained according to Hurd and Puterbaugh, THIS JOURNAL, **52**, 950 (1930).

(3) D'Ans and Friedrich, *Z. anorg. Chem.*, **73**, 345 (1912).

(4) Müller and Holder, *Z. anal. Chem.*, **84**, 410 (1931).

(5) Lubarski and Dikowa, *ibid.*, **81**, 450 (1930).

(6) *Cf.* H. Ährle, *Z. angew. Chem.*, **22**, 1713 (1909).

(7) Th. S. Price [*J. Chem. Soc.*, **89**, 53 (1906)] noted that on the acid side, even at boiling temperature, the complete acid value is slow to be reached.

(8) G. Toennies, THIS JOURNAL, **56**, 2198 (1934).

(9) *Cf.* footnote 2a. The chief difficulty in maintaining low temperature and achieving intimate mixing of the components—both essential—appears at a stage when an appreciable part of the persulfate has been added and when rather suddenly the reaction spreads through the mixture as evidenced by rising temperature and stiffening of the whole mass. Previous reports do not appear to have mentioned this phenomenon.

TABLE I

PERMONOSULFURIC ACID SOLUTIONS. SUMMARY OF PREPARATIONS

No.	$K_2S_2O_8$ mml. used	Molar ratio $\frac{H_2SO_4{}^a}{K_2S_2O_8}$ used	Solvent used	Yield in soln., % of peroxygen used H_2SO_5	Total per-O	Concn. in soln. Free acid, normal. (N_A)	H_2SO_5, molarity (M_0)	Acid in residue, % of total potential acid[b]
1	420	4.65	500 cc. ethanol	75	78	5.8	0.60	20
2	410	4.65	500 cc. isopropanol	53	55	6.4	.51	32
3	37	4.65	50 cc. isoamyl alcohol	54	66	5.1	.51	40
4–7	100–230	3.00	Isoamyl alcohol[c]	41 ± 4	51 ± 5	4.4 ± 0.2	.53 ± 0.05	47 ± 4
8	370	4.65	450 cc. acetonitrile	44	52	5.9	.31	16

[a] The sulfuric acid used was of 92.5% concentration in preparations 1–7, and of 96% in number 8. [b] *I. e.*, including that from $K_2S_2O_8 + H_2O \longrightarrow K_2SO_4 + O + H_2SO_4$. [c] The amount used was equal in cc. to the mml. $K_2S_2O_8$ used, *e. g.*, 230 cc. for 230 mml. of $K_2S_2O_8$.

Stability and Reactions. (a) in **Alcohols.**—In order to obtain some initial information on the factors of stability of, and the nature of the reactions involved in, alcoholic solutions of the peracid, the ethanol solution described above and two ethanolic dilutions, one of one-half and one of one-quarter the original concentration, were each divided into three portions, and of these one was kept at room temperature (about 26°), one in a refrigerator (about 2°) and one in the low temperature compartment of the refrigerator (about −12°). On each of these nine portions periodical determinations were made of permonosulfuric acid, total peroxygen, free acidity and total acidity. The results are given in Fig. 1. A comparison of plots 1, 2 and 3 indicates that the rate of decomposition of permonosulfuric acid is higher in presence of higher acid concentration. Since in none of the solutions formation of free oxygen ($2H_2SO_5 \longrightarrow 2H_2SO_4 + O_2$, $H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O + O_2$ or $2H_2O_2 \longrightarrow H_2O + O_2$)—the cause of decreasing strength in pure aqueous solutions—was perceptible, and since the characteristic odor of ethyl acetate became very noticeable as the peracid disappeared from the alcoholic solutions, the decrease in total peroxygen may be attributed to formation of acetic acid which in the presence of the prevailing high concentrations of acid and

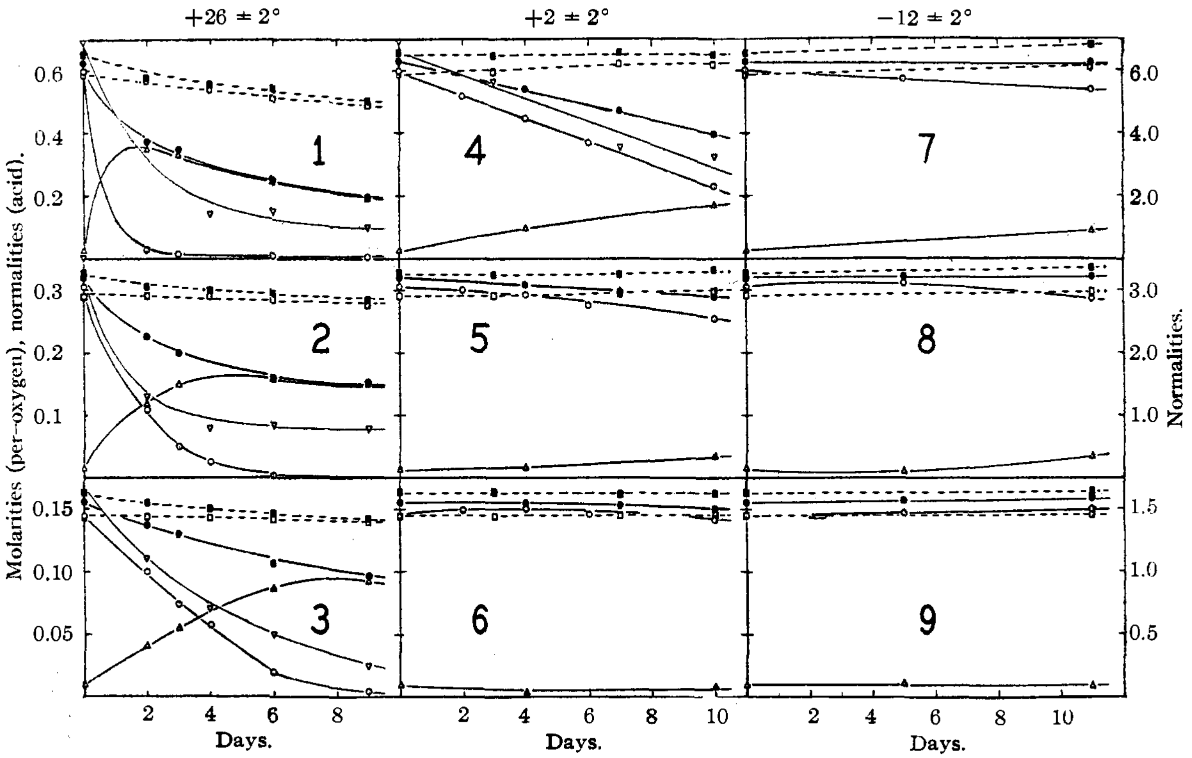

Fig. 1.—The behavior of ethanolic solutions of permonosulfuric acid. Full lines refer to the left ordinate scale, broken lines to the right ordinate scale. "Molarity (peroxygen)" is used to signify number of g.-atoms of active oxygen per 1000 cc. ■, total acid; □, free acid; ▽, acid formed by alkaline boiling (total minus free acid); ●, total peroxygen; ○, permonosulfuric acid; △, peroxygen other than H_2SO_5 ("non-SO_5," *i. e.*, total peroxygen minus permonosulfuric acid). The plots of the nine individual experiments are numbered 1 to 9.

alcohol would be expected to esterify to a large extent. On account of attending difficulties[10] quantitative determination of the ester was not attempted in this exploratory work. Assuming that the reaction $H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$ is substantially irreversible as it is in aqueous solution[11] the "non-SO_5 peroxygen" would consist of one or several of the possible neutral peroxides (hydrogen peroxide, mono- or diethyl peroxide). The oxidation to acetic acid (as measured by the decrease in total peroxygen) is effected by permonosulfuric acid as well as by the "non-SO_5" fraction (although at a lower rate by the latter) as evidenced in plots 1, 2 and 3 by the continued decrease in total peroxygen after the permonosulfuric acid has become nearly zero. The decrease in total acidity which is evident at room temperature is presumably due to formation of ethylsulfuric acid, which is highly resistant to alkaline hydrolysis (Beilstein), while an increase in free acidity, visible in plot 4, may be attributed to hydrolysis of residual persulfuric acid. The main practical result expressed in Fig. 1 is the observation that at about −10° temperatures are approached at which all other reactions become negligible compared with the transfer of oxygen atoms from H_2SO_5 to "non-SO_5" combinations, while even the speed of this reaction drops below one per cent. per day.

Results quite similar to those shown for the ethanol solution were obtained with regard to the stability of the isopropyl alcohol solution (Table I). The concentrated solution showed at −12°, over a period of nine days, a decrease in permonosulfuric acid of 1.1% per day, while all other changes were negligible. In an isopropyl alcohol dilution to one-quarter the original strength the corresponding rate of decrease was 0.5% per day. The stability of the peracid in similar isoamyl alcohol solutions was somewhat less; solutions nos. 4–7 (Table I) showed rates of decrease of 2.5-3.9% per day. However, the effect of acidity on the stability is also marked here. Table II shows results obtained on a solution made by adding 4.7 cc. of a concentrated permonosulfuric acid solution, prepared according to method B, to isoamyl alcohol of −12° and making up to 100 cc. The average rate of decrease of the peracid is about 0.8% per day, while the sum of $H_2SO_5 + H_2O_2$ decreased only by 4.7% over the whole ninety day period, indicating that the main reaction occurring is a shift of oxygen between permonosulfuric acid and hydrogen peroxide.

TABLE II

STABILITY OF PERMONOSULFURIC ACID IN ISOAMYL ALCOHOL at −12°

Days	−4[a]	0	5	13	34	90
H_2SO_5, M	0.502	0.534	0.514	0.482	0.397	0.258
H_2O_2, M	.102	.042	.060	.087	.166	.291
H_2SO_4, M	.167	.116				
H_2O, M	.243					

[a] This column shows the values calculated from the analytical data and the weighed amount used, of the concentrated H_2SO_5 solution which was made and analyzed four days prior to the amyl alcoholic solution.

(b) **In Acetonitrile.**—In the acetonitrile preparation (solution no. 8, Table I) the total recovery of the peroxygen used (including that contained in the solid residue) was 98%. The stability of the resulting solution is apparent from the data of Table III. In contrast to the rapid decomposition at room temperature[12] the solution is of useful stability at −13°.

TABLE III

STABILITY OF PERMONOSULFURIC ACID IN ACETONITRILE

Days	t	H_2SO_5 M_0	Total per–O M_0	Free acid N_A	Total acid N_A
0	30 ± 2°	0.317	0.378	5.88	6.30
0.25[a]		.014			
1[b]		.009	.229	5.34	6.44
2[c]		.004	.224	4.93	6.32
10[d]		.000	.185		
0	−13 ± 2°	.317	.378	5.88	6.30
2		.326			
4		.328		5.83	6.20
10			.330		
44		.19			
70		.13			

[a] Due to heat of reaction temperature of flask has risen to about 40°. [b] Orange color and odor of acetic acid present. [c] Also odor of sulfur dioxide present. [d] On further standing gradually a heavy brown oil settles out, leaving a colorless supernatant liquid of pure acetonitrile odor.

(c) **Explosions.**—In studying the effect of the medium it became desirable to use at least one secondary and one tertiary alcohol for comparison with the primary ones. An advantage expected from these alcohols was slower esterification with sulfuric acid and concomitantly slower formation of water the presence of which is undesirable for some purposes. The alcohols chosen were *s*-methylisobutylcarbinol (Eastman, practical) and *t*-ethyldimethylcarbinol (Eastman).[13] Especially with regard to the tertiary one there was the additional expectation of greater resistance against oxidation by permonosulfuric acid, based on determinations of oxidation velocities by alkaline permanganate, of Tronov, Lukanin and Pavlinov[14] who for the tertiary amyl alcohol reported a velocity constant of about $^1/_{500}$ of that of isoamyl alcohol, while they found the oxidation velocity of secondary alcohols generally a little higher than that of the primary ones. Addition of concentrated peracid (made by method B) to 9.5 cc. of 1.1 M H_2SO_4 (using 99% H_2SO_4) in methylisobutylcarbinol at −10°, to make a 0.50 M H_2SO_5 solution, was done without difficulty, while in the corresponding operation using ethyl-

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(10) Indications were obtained that the acid which is liberated by alkaline boiling and which results from decomposition of H_2SO_5 and $H_2S_2O_8$ as well as from saponification of ethyl acetate, may be further increased by oxidation of alcohol to acid, occurring during the alkaline boiling.

(11) Palme, *Z. anorg. allgem. Chem.*, **112**, 47 (1920).

(12) It seems probable that the rapid decomposition is linked to the acid catalyzed hydrolysis of acetonitrile [*cf.* Lavine and Toennies, *J. Biol. Chem.*, **101**, 727 (1933)].

(13) Their relative speeds of esterification were determined by measuring the change in acidity at room temperature of small samples containing anhydrous sulfuric acid at a concentration of approximately twice molar. After four days the free acidity of the solution of the primary alcohol had diminished 32%, that of the secondary 15%, while that of the tertiary was substantially unchanged, although after three days an initial drop of about 5% had taken place. We can suggest no reason for this subsequent increase in free acidity.

(14) Tronov, Lukanin and Pavlinov, *J. Russ. Phys.-Chem. Soc.* **59**, 1173 (1927); *cf. C. A.*, **22**, 3336 (1928).

dimethylcarbinol an explosive reaction occurred on addition of few drops of the concentrated peracid, in spite of careful cooling. After thorough purification—by twice allowing to stand overnight with an excess of concentrated permanganate solution, washing, drying with barium oxide and fractionating (collected between 101.6° and 102.5°)—this tertiary alcohol still showed the same explosive tendencies, indicating that impurities can hardly be considered responsible for this behavior. A more dramatic demonstration of potential dangers occurred when a repetition, with fourfold amounts, of the above methylisobutylcarbinol experiment resulted in a violent detonation. Local overheating leading to a cumulative reaction evidently represents a real danger, at least in this particular alcohol. The following experiments throw some additional light on the danger factors. 0.30 cc. of concentrated peracid (11.7 M H_2SO_5, 3.3 M H_2SO_4, 0.6 M H_2O_2, 5.3 M H_2O) was added to 4 cc. of each of the following, cooled in freezing mixture: (a) isoamyl alcohol, (b) 4 M H_2SO_4 (99.4%) in isoamyl alcohol, (c) methylisobutylcarbinol, (d) 4 M H_2SO_4 in methylisobutylcarbinol. Of the resulting solutions (c) exploded after about one minute and (d) a little later, both while remaining in the freezing mixture. (a) and (b) were taken to room temperature after fifteen minutes, and now (a) exploded after several minutes while (b) did not explode. Obviously the primary $C_5H_{11}OH$ is less reactive than the secondary $C_6H_{13}OH$ and the latter in turn is more stable than the tertiary $C_5H_{11}OH$. The apparent reduction of explosibility by the presence of considerable sulfuric acid (about 37.5%) may be caused by the dilution of the organic component. It should be noted that the permonosulfuric acid concentration used (about 0.8 M) as well as the sulfuric acid concentration are considerably higher than those encountered in the solutions described in the earlier part of this paper, and in which no explosive tendencies were ever observed, even though considerable quantities were handled.

The writer wishes to express his appreciation of the assistance rendered by Dr. Mary A. Bennett in some phases of the experimental work.

Summary

Methods for obtaining solutions of permonosulfuric acid in some of the lower alcohols, including isoamyl alcohol, and in acetonitrile have been described. Examples illustrating the nature of the slow decompositions taking place in such solutions have been given and it has been shown that at −12° solutions containing as much as 0.6 M H_2SO_5 are of convenient stability. Attention is called to the possibility of explosive reactions with secondary and tertiary alcohols, and generally in cases of too high concentrations of the peracid.

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A New Method for the Preparation of Permonophosphoric Acid[1]

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Permonophosphoric acid since its discovery in 1910 by Schmidlin and Massini[2] has received little attention although it is distinguished by a remarkable oxidizing power (lower manganese salts are oxidized, in the cold, to permanganate). The method of Schmidlin and Massini, consisting in gradually combining phosphoric anhydride and concentrated hydrogen peroxide in very small portions, is difficult on account of the violence of the interaction, and uncertain as to result in spite of its tediousness. The only other method proposed by Fichter and associates,[3] produces by anodic oxidation mixtures of alkali salts of H_3PO_5 and $H_4P_2O_8$ in solutions of potassium fluoride and therefore is of limited usefulness. The present experiments were undertaken with a view of simplifying the production of this interesting compound by moderating the reaction between phosphoric anhydride and hydrogen peroxide through the use of suitable inert diluents for the latter.

Of three solvents studied, ether, isoamyl alcohol and acetonitrile, only the last one gave satisfactory results. Acetonitrile is completely inert against phosphoric anhydride and it can be used to make solutions of hydrogen peroxide of high concentration and high stability.[4] In two parallel experiments, in which the components were used in ratios approximately corresponding to the assumed reaction

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5 \qquad (I)$$

phosphoric anhydride (5.55 and 5.18 mml., respectively,) was suspended in 1.5 cc. of acetonitrile (Merck reagent) and at low temperature (freezing mixture) an acetonitrile solution (1.10 and 1.05 cc.) containing hydrogen peroxide[5] (12.94 and 12.35 mml.) and water (4.03 and 3.84 mml.) was added slowly. Besides, 0.30 cc. of acetonitrile was

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[1] Aided by a grant for fundamental research from E. R. Squibb and Sons.

[2] Schmidlin and Massini, *Ber.*, **43**, 1162 (1910).

[3] Fichter and associates, *Helv. Chim. Acta*, **1**, 297 (1918); **2**, 3 (1919); S. Husain and J. R. Partington, *Trans. Faraday Soc.*, **24**, 235 (1928).

[4] G. Toennies and M. Elliott, results to be published shortly in THIS JOURNAL.

[5] Hydrogen peroxide of 80 to 90% concentration was prepared according to Hurd and Puterbaugh, THIS JOURNAL, **52**, 950 (1930).