TABLE III

ACTIVITY COEFFICIENTS RECALCULATED FROM $\Delta\varphi$

m	AlCl$_3$	ScCl$_3$	YCl$_3$	LaCl$_3$	CeCl$_3$	PrCl$_3$	NdCl$_3$	SmCl$_3$	EuCl$_3$
				Activity	Coefficients				
0.05	0.436	0.412	0.417	0.417	0.394	0.402	0.403	0.408	0.412
.1	.384	.357	.357	.356	.338	.343	.344	.351	.355
.2	.348	.322	.317	.312	.299	.302	.302	.310	.315
.3	.338	.315	.307	.298	.286	.289	.290	.300	.303
.4	.357	.321	.309	.295	.285	.286	.289	.299	.303
.5	.378	.334	.318	.303	.290	.290	.294	.304	.308
.6	.406	.353	.332	.312	.300	.298	.303	.316	.322
.7	.442	.378	.350	.324	.313	.300	.316	.331	.338
.8	.487	.409	.373	.340	.330	.327	.334	.351	.359
.9	.542	.447	.402	.362	.349	.347	.354	.375	.384
1.0	.610	.492	.436	.387	.372	.371	.380	.403	.413
1.1	.689	.544	.476	.416	.399	.399	.410	.436	.447
1.2	.815	.604	.524	.449	.430	.433	.445	.475	.486
1.3	.918	.674	.580	.488	.467	.471	.485	.518	.533
1.4	.935	.755	.644	.533	.509	.514	.531	.569	.587
1.5	1.253	.850	.718	.583	.558	.562	.570	.628	.649
1.6	1.610	.961	.804	.639	.614	.618	.642	.695	.720
1.7	1.773	1.089	.904	.703	.681	.681	.710	.771	.802
1.8	2.131	1.238	1.023	.776	.758	.753	.790	.859	.897
1.9	...	1.408	1.164	.859	.846	.836	.881	.961	1.009
2.0	...	...	1.330	.954	.946	.929	.984	1.079	1.140

Summary

1. The osmotic coefficients of samarium and europium chlorides have been determined in aqueous solution at 25° by the isotonic method.

2. A new method is described for the smoothing of osmotic coefficients and the calculation of activity coefficients.

3. The activity coefficients of aluminum, scandium, yttrium, lanthanum, cerous, praseodymium, neodymium, europium and samarium chlorides have been calculated by a new method.

4. The activity coefficients of lanthanum chloride have been compared with existing data.

The Relation between the Oxidizing Action and Catalytic Decomposition of Concentrated Hydrogen Peroxide. I. Osmium Tetroxide as a Catalyst in the Oxidation of Acetic and Propionic Acids

BY LUTHER M. FOSTER AND JOHN H. PAYNE

The apparent relationship between the rate of decomposition and the oxidizing action of hydrogen peroxide has generally been explained by assuming that atomic oxygen liberated in the decomposition is the active oxidizing agent. The unique action of hydrogen peroxide upon many organic compounds has shown that such is not the case.[1,2,3]

In many instances, for example in the addition of hydroxyl groups to double bonds, the hydrogen peroxide molecule enters into the reaction. It is possible, nevertheless, that the same catalyst may increase the speed of both the oxidation reaction as well as the decomposition of the hydrogen peroxide.

In order to study this problem, the oxidation of acetic and propionic acids by 60% hydrogen peroxide in the presence of varying amounts of osmium tetroxide as a catalyst was investigated. The method used made possible the simultaneous quantitative determination of the extent of the oxidation, as indicated by the amount of carbon dioxide formed, and the decomposition of the peroxide, as shown by the evolution of oxygen. Osmium tetroxide was chosen for study because it is one of the most active catalysts for the de-

(1) Fry and Payne, THIS JOURNAL, 53, 1973 (1931).
(2) Milas and Sussman, ibid., 58, 1302 (1936).
(3) Milas and Sussman, ibid., 59, 2345 (1937).

composition of hydrogen peroxide.[4] The reagent likewise has been found to be effective as an oxidative catalyst.[2,3,5,6] Acetic acid and propionic acid were studied because of their resistance to oxidation. In the absence of catalysts, they are reported to be only slightly attacked by hydrogen peroxide.[7,8] Consequently the effect of the catalyst should be distinguished easily.

Experimental

Reagents.—The hydrogen peroxide used was of approximately 60% concentration. It was prepared by flash vacuum distillation of commercial 30% hydrogen peroxide.[9] The concentrated reagent was stabilized with 100 mg. of sodium pyrophosphate and 20 mg. of sodium stannate per liter of solution, and pH adjusted to 4.1 with a trace of sulfuric acid. Special precautions were taken to keep the peroxide free from foreign substances. The reagent showed no change in composition over a period of several months. The acetic and propionic acids were Eastman Kodak Co. White Label. They were freshly redistilled just prior to use. The osmium tetroxide catalyst was prepared by making a solution of known concentration of the Eastman White Label reagent in redistilled water.
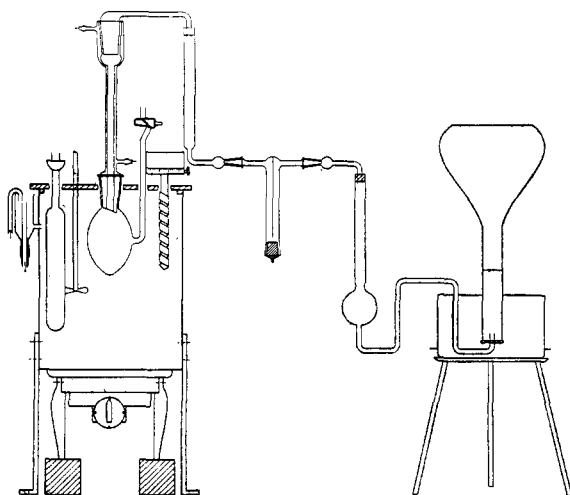

Fig. 1.—Oxidation apparatus.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1. Constructed entirely of Pyrex glass, it consisted of a 100-ml. reaction flask connected by ground glass joints to a condenser, thence to a drying tube, weighed ascarite absorber, second drying tube in train, and finally to a gas-collecting flask. The reaction flask

(4) Chugaev and Bikerman, Z. anorg. allgem. Chem., 172, 229 (1928).

(5) Criegee, Ann., 522, 75 (1936).

(6) Hofmann, Ber., 45, 3329 (1912).

(7) Bernhauer and Nistler, Biochem. Z., 205, 230 (1929).

(8) Hatcher and co-workers, Trans. Roy. Soc. (Can.), 20, 407 (1926).

(9) The hydrogen peroxide was donated by the R. and H. Chemicals Division of E. I. du Pont de Nemours and Company.

was immersed in a constant temperature-bath which could be regulated to ±0.1°.

Procedure.—The acid was measured directly into the reaction flask which was cooled in an ice-bath. Hydrogen peroxide, in an approximate molar ratio of fifty to one, was then pipetted into the flask and the catalyst added. The flask was connected immediately to the apparatus and the entire train flushed out thoroughly with oxygen-free nitrogen. The gas-collecting flask was then attached and the thermostat brought to a temperature of 100°. The reaction was allowed to proceed at this temperature for four hours.

At the end of the four-hour period, the apparatus was again flushed with nitrogen and the flushing gas collected in the gas-collecting flask. The reaction flask was removed and cooled. Aliquot portions were analyzed for total acidity by titration with standard base, and for unused hydrogen peroxide by titration with standard permanganate. The reaction mixture was tested also qualitatively for the presence of oxalic and formic acids. The amount of carbon dioxide evolved was determined by the gain in weight of the ascarite absorber. Analysis of the collected gas showed oxygen and nitrogen as the only constituents. Oxygen was determined by absorption in Fieser's solution.[10]

Data.—The data obtained for acetic acid are given in Table I. Similar data for propionic acid are given in Table II. Neither oxalic acid nor formic acid was found in the reaction mixture from any of the runs.

TABLE I

OXIDATION OF ACETIC ACID BY HYDROGEN PEROXIDE IN THE PRESENCE OF OSMIUM TETROXIDE

0.00648 mole acetic acid; 0.365 mole hydrogen peroxide.

OsO_4 mole × 10^{-7}	H_2O_2 found, mole	Acid found, equiv.	CO_2 found, mole	O_2 found, mole
None	0.347	0.00642	0.00010	0.0048
1.3	.331	.00632	.00037	.0121
2.5	.318	.00630	.00044	.0182
5.0	.305	.00626	.00053	.0246
10.0	.289	.00602	.00074	.0344
20.0	.249	.00593	.00094	.0564

TABLE II

OXIDATION OF PROPIONIC ACID BY HYDROGEN PEROXIDE IN THE PRESENCE OF OSMIUM TETROXIDE

0.00653 mole propionic acid; 0.365 mole hydrogen peroxide.

OsO_4 mole × 10^{-7}	H_2O_2 found, mole	Acid found, equiv.	CO_2 found, mole	O_2 found, mole
None	0.346	0.00662	0.00016	0.0101
1.3	.326	.00622	.00059	.0185
2.5	.309	.00594	.00151	.0255
5.0	.279	.00562	.00309	.0382
10.0	.257	.00466	.00424	.0473
20.0	.219	.00432	.00627	.0624

Discussion

It will be noted in Tables I and II that, under the conditions studied, the oxidation of both

(10) Fieser, THIS JOURNAL, 46, 2639 (1924).

acetic and propionic acids in the absence of a catalyst is almost negligible. Thus, as measured by the carbon dioxide evolved, only 0.7% of the acetic acid and 0.8% of the propionic acid is oxidized in four hours at 100°.

The oxidation of acetic acid increases only slightly with increasing amounts of osmium tetroxide. The oxidation of propionic acid, however, increases much more rapidly. This comparison is shown graphically in Fig. 2, in which the carbon dioxide evolved is plotted against the amount of osmium tetroxide used. The great resistance of acetic acid to oxidation is indicated by the very gradual slope as compared with the much greater slope for propionic acid. It is interesting to note that the amount of carbon dioxide evolved bears a linear relationship to the amount of catalyst, where the latter concentration exceeds 5×10^{-7} mole. The curves indicate that this relationship probably would continue to exist at higher concentrations of the catalyst.

Intermediate products of the oxidation of acetic acid would not be expected in the reaction mixture, since they all should be more readily oxidized than the acid itself. The absence of formic acid, and the fact that two moles of carbon dioxide were formed for every mole of acetic acid used, as shown in Table I, substantiates this. The oxidation of propionic acid in the presence of higher concentrations of the catalyst resulted in a considerable decrease in acid concentration. This decrease was more than could be accounted for by the intermediate formation and subsequent oxidation of acetic acid. It is probable, therefore, that the oxidation of propionic acid under these conditions does not involve the formation of acetic acid.

Simultaneously with the oxidation reaction, decomposition of hydrogen peroxide into molecular oxygen and water increases with increasing amounts of osmium tetroxide.

A comparison of data in Table I and Table II will show that an increasing rate of oxidation in
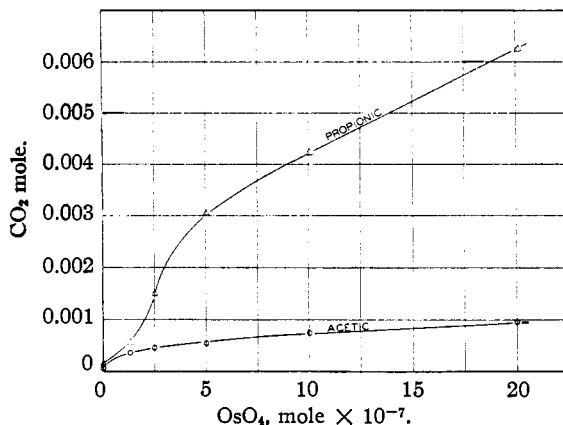

Fig. 2.—Effect of osmium tetroxide upon the oxidation of acetic and propionic acids by hydrogen peroxide, as measured by carbon dioxide evolved.

each case is paralleled by an increase in the rate of the decomposition of the hydrogen peroxide. Thus it is evident that in the case of osmium tetroxide there is a parallel relationship between its catalytic effect upon both oxidation and decomposition. Similar behavior might be expected with other catalysts.

Summary

The oxidation of acetic and propionic acids by 60% hydrogen peroxide in the presence of varying amounts of osmium tetroxide has been investigated.

1. In the absence of the catalyst, the oxidation of both acetic and propionic acid is negligible after four hours at 100°.

2. In the presence of osmium tetroxide the oxidation increases approximately linearly with the amount of catalyst. Propionic acid is oxidized more completely, and its rate of oxidation increases more rapidly than does that of acetic acid.

3. The oxidation of the acids and the decomposition of the hydrogen peroxide are both catalyzed by osmium tetroxide in a parallel manner.