The Convenient Preparation of Per-acids

By Frank P. Greenspan

The commercial availability of concentrated hydrogen peroxide (90% by weight) has now made possible a convenient, safe and rapid preparation of per-acids by simple interaction with aliphatic acids in the presence of 1% sulfuric acid as a catalyst. The procedure used is substantially the same as that employed by D'Ans and Frey[1,2] in their classical study of per-aliphatic acids.

Because of interest in the aliphatic per-acids for oxidation and hydroxylation reactions,[3] an investigation has been made of the comparative rate of per-acid formation with concentrated hydrogen peroxide (90%) and more dilute hydrogen peroxide (30%). With 90% hydrogen peroxide, it has been possible to prepare 46.0% peracetic acid solutions and 35.8% performic acid solutions, six- to seven-fold higher concentrations than obtained with previously used procedures employing 30% hydrogen peroxide. Results with 90% hydrogen peroxide check well with those obtained by D'Ans and Frey[1,2] using specially prepared 98–100% hydrogen peroxide.

Experimental

Peracetic Acid Formation with 90% Hydrogen Peroxide.—Ten grams of glacial acetic acid was added to specially cleaned volumetric flasks containing 0.11 ml. of concentrated sulfuric acid (1% concentration on total contents). The flask was immersed in a water-bath, agitated with an air stirrer, and maintained at 22–23°; 9.1 g. of 90% hydrogen peroxide was then added to the flask contents—the mole ratio of hydrogen peroxide to acetic acid being 1.5 to 1.0 as for succeeding experiments; 1 ml. aliquots were withdrawn at intervals, diluted to 100 ml. with ice cold water, and a 20-ml. aliquot titrated in the cold for hydrogen peroxide and peracetic acid content, using a modified procedure of D'Ans and Frey.[1,2] Results are plotted as the number of moles of peracid formed per mole aliphatic acid used *vs.* time, Curve 1. At the end of four hours, peracetic acid concentration is 44.4%, rising to a maximum of 46.0% within twelve to fifteen hours. D'Ans and Frey obtained an equilibrium within twelve to sixteen hours at a peracetic acid concentration of 51.5%.

Peracetic Acid Formation with 30% Hydrogen Peroxide.—Procedure was same as above using 28.8 g. of 30% hydrogen peroxide and 0.4 g. of sulfuric acid, Curve 2. Maximum peracetic acid concentration is 8.6% reached in eighty to ninety hours.

Performic Acid Formation with 90% Hydrogen Peroxide.—The procedure is same as for peracetic acid: 23.0 g. of formic acid (98–100%) reacted with 28.4 g. of 90% hydrogen peroxide in the presence of 1% sulfuric acid, Curve 3. Maximum performic acid concentration is 35.8% reached within thirty minutes compared to that of 48% reported by D'Ans and Frey in two hours.

Performic Acid Formation with 30% Hydrogen Peroxide.—The procedure is same as above using 9.2 g. of formic acid and 33.7 g. of 30% hydrogen peroxide in the presence of 1% sulfuric acid, Curve 4. Maximum performic acid concentration is 4.7% reached within two hours.

Stability and Storage.—Peracetic acid prepared from 90% hydrogen peroxide shows surprisingly good storage stability—75% of the peracid remaining after forty-nine days at room temperature for a typical unstabilized preparation, with still greater stabilities being shown by specially stabilized solutions (a sample containing 100 pts. per million of sodium pyrophosphate when tested after forty-nine days showed 94% of the original peracetic acid remaining). Performic acid is less stable, gassing being noticeable after a few hours of standing, and the effective concentration showing a definite decline in two hours. Decomposition of the peracids is exothermic. It is therefore advisable to maintain peracetic acid during formation and storage below 30°.

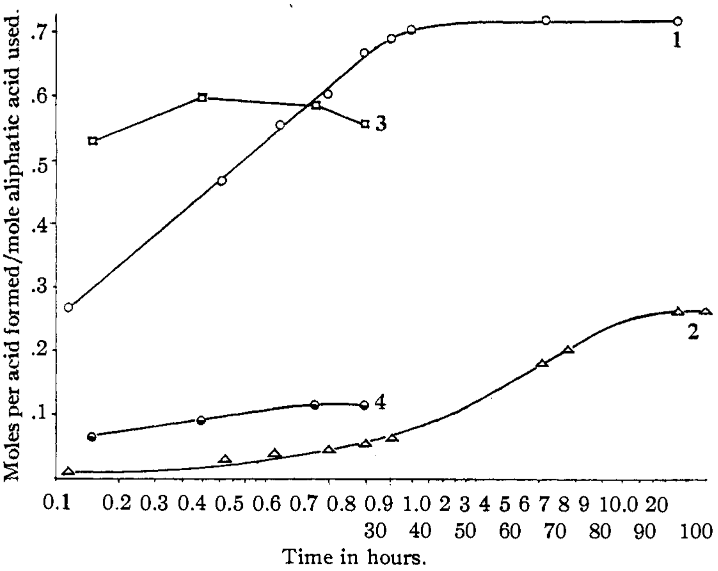

Fig. 1.—Curve 1, peracetic formation with 90% hydrogen peroxide; curve 2, peracetic formation with 30% hydrogen peroxide; curve 3, performic formation with 90% hydrogen peroxide (showing some decomposition); curve 4, performic formation with 30% hydrogen peroxide.

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[1] D'Ans and Frey, *Ber.*, **45**, 1845 (1912).

[2] d'Ans and Frey, *Z. anorg. Chem.*, **84**, 145–164 (1913).

[3] Swern, Billen, Findley and Scanlan, This Journal, **62**, 2305 (1940).

β,β'-Dipyridyl Ketone

By Fred Linsker and Ralph L. Evans

Although no dipyridyl ketone has been reported to date, mention is made in the older literature[1] of a high-boiling base which was obtained in small amount in the dry distillation of calcium nicotinate. From 20 g. of the calcium salt was obtained 0.6 g. of a new base which was analyzed as the chloroplatinate and at that time believed to be a dipyridyl compound.

In our search for a suitable method of preparing β,β'-dipyridyl ketone we repeated Laiblin's experiment and confirmed his observations. A some-

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[1] Laiblin, *Ann.*, **196**, 160 (1879)