

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Cycloalkanone Peroxides. II. Nature of Peroxides Produced by Oxidation of Cyclopentanol

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RECEIVED APRIL 3, 1954

The peroxides produced by photo-initiated liquid phase oxidation of cyclopentanol are qualitatively similar to those produced from cyclohexanol, except that they dissociate in solution to a greater extent. Reaction of these peroxides with ferrous sulfate produced sebacic acid in poor yields.

The previous paper in this series¹ has described oxidation of cyclohexanol to "cyclohexanone peroxides" and reaction of the latter with ferrous ion to yield 1,12-dodecanedioic acid. In the present paper, comparable reactions starting with cyclopentanol will be discussed.

Liquid phase oxidation of cyclopentanol by oxygen was carried out in a low temperature photo-initiated system. Photo-initiated oxidation of cyclic alcohols has been described by Milas.² In our studies, a marked increase in oxidation rate was obtained by operation in the presence of the light-sensitive benzoin. Calcium carbonate was found to promote peroxide stability in this technique; results obtained are summarized in Table I. Identical results were obtained in quartz and in Pyrex brand glass equipment. The autocatalyzed oxidation of cyclopentanol was not evaluated as it was felt that its boiling point (139°) was too low for satisfactory oxidation at atmospheric pressure.

TABLE I

PHOTO-CATALYZED OXIDATION OF CYCLOPENTANOL AND OF CYCLOHEXANOL

1% benzoin, 2-5% CaCO₃, "RS" Sunlamp

Compound	Temp., °C.	Initial oxidn. rate ^a	Peak conv. to peroxide, % ^b	Time of reach peak conv.
Cyclopentanol	60	0.8	17	3 days
	100	4.0	16	9 hr.
Cyclohexanol	60	0.8	19	2 days
	100 ^c	3.5	12	5 hr.

^a % conv. to peroxide/hour. ^b Moles peroxide in product per 100 moles original alcohol. ^c At 9.2% conversion to peroxide, yield of peroxide/O₂ = 66%, yield of cyclohexanone plus cyclohexanone peroxides/cyclohexanol = 76%.

Hydrogen peroxide was apparently the chief peroxidic product of the oxidation of cyclopentanol,³ as shown by countercurrent distribution analysis, and was produced to a much greater extent than in the oxidation of cyclohexanol. Thus, the equilibrium point in the reaction (ketone + H₂O₂ ⇌ "ketone peroxide") lies further to the right with a six-membered than with a five-membered ring. This observation substantiates current theory on strain in cycloaliphatic rings⁴ which postulates

(1) N. Brown, *et al.*, *THIS JOURNAL*, **77**, 1756 (1955).

(2) N. A. Milas, U. S. Patents 2,115,206; 2,115,207 (1938).

(3) This discussion concerns oxidation products which presumably have had sufficient time for peroxide equilibration to take place in the solvent.

(4) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *THIS JOURNAL*, **73**, 212 (1951). Note also dissociation constants: cyclopentanone cyanohydrin 0.0149, cyclohexanone cyanohydrin 0.0009 (V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 174).

that the tricoordinate carbon is favored in five-membered rings, and the tetracoordinate in six-membered rings.

In the oxidation of cyclopentanol, hydrogen peroxide and free ketone were apparently the sole major reaction products at low conversion. As the conversion increased, decomposition of some peroxides caused a progressive increase in the ratio of total equivalent ketone to peroxides. This, along with concentration effects, displaced the peroxide equilibrium with the formation of gradually increasing amounts of "organic peroxide," as determined by single-stage solvent partition with water (Fig. 1). A similar trend occurred in the oxidation of cyclohexanol; however, appreciable amounts of organic peroxides were present even at low conversions.

Addition of cyclopentanone to the cyclopentanol oxidation product caused a gradual increase in "organic peroxide" content. However, not only was the equilibrium point less favorable than in the C₆-series, but also the rate of reaching equilibrium was slower.

Reaction of the crude oxidation product with methanolic ferrous sulfate yielded sebacic acid. Yields were low, as would be predicted from peroxide analytical data. Direct reaction gave 8-18% yield (Table II). The benefits of preliminary treatment with cyclopentanone on coupling yields were apparent even using ferrous sulfate reagent, as might be expected considering the slow peroxide equilibration rate. Even so, the best yield obtained was only 24%. Ketone treatment was carried out in the presence of sulfuric acid catalyst.

TABLE II

REDUCTIVE COUPLING OF PEROXIDES IN CRUDE PRODUCT FROM OXIDATION OF CYCLOPENTANOL

Oxidation conditions: ultraviolet light, 1% benzoin, 2-5% CaCO₃, 12-17% conversion to peroxides

Oxidation temp., °C.	Product pretreatment before coupling	Org. peroxide, % ^a	Yield, % ^b	Yield from C ₆ , % ^c
100	None	23	8	..
100	Ketone treated	76	24 ^d	47 ^e
60	None	57	18	36

^a By single-stage solvent extraction following pretreatment. ^b Of sebacic acid, based on total peroxide. ^c Of 1,12-dodecanedioic acid, from the peroxides derived from cyclohexanol under comparable conditions. ^d 0.1% H₂SO₄ catalyst in ketone treatment. ^e No catalyst in ketone treatment.

Experimental Details

Cyclopentanol was redistilled at atmospheric pressure through a three-foot packed column.

Oxidation of Cyclopentanol.—Reactions were carried out in 25-mm. diameter Pyrex cylindrical reactors equipped with a sample line at the bottom. Oxygen was introduced through a fine fritted glass disc. The tube was equipped with a reflux condenser. Light and heat were supplied by a Westinghouse 275-watt RS type sunlamp with a reflector behind the reactor. In a typical oxidation, 33.0 g. of cyclopentanol, 1.65 g. of calcium carbonate and 0.33 g. of benzoin were processed with 50 ml. per min. of O₂ at 100°. Analytical data are shown in Table III.

TABLE III
PHOTO-INITIATED OXIDATION OF CYCLOPENTANOL

Time, hr.	Peroxide, millimoles/g.	Ketone, ^a meq./g.	Acid, meq./g.	Organic peroxide, % of total peroxide
1.67	0.550
3.25	0.975	1.275	0.129	14
4.92	1.340
9.9	0.655	2.60	1.09	45
21	0.037	3.23	1.60	..

^a By steam distillation and analysis of distillate by hydroxylamine.

Separation of Peroxides from Crude Cyclopentanol Oxidation Product by Countercurrent Distribution.—This was carried out in a 24-tube Craig machine.⁵ A product sample of 10% conversion to peroxides was used, with mutually saturated cyclopentanol and water as the solvent pair. After 18 transfers, there were three peroxide peaks, the first at $Q = 77\%$ (75% of total), the second, poorly resolved, at $Q = 40\%$ (15% of total), and the third at $Q = 10\%$ (10% of total) where $Q = 100C_w/(C_w + C_o) =$ percentage of peroxide in water phase. A control experiment with hydrogen peroxide showed $Q = 77\%$. Over-all distribution of peroxide corresponded to $Q = 60.6\%$ compared to 56.0% in a single stage extraction, showing very little hydrolysis during the distribution experiment.

Analysis for "organic peroxides" in oxidation products was carried out by single-stage extraction with an equal volume of water followed by titration of equal volume aliquots for peroxide. Calculations were made on the basis of $Q = 77\%$ (81% in cyclohexanol) and 0% for hydrogen peroxide and "organic peroxide," respectively. The latter figure is based on the solubility of commercial "cyclohexanone peroxide." For example, $Q = 38.5\%$ is equivalent to 50% "organic peroxide." It is apparent that the significance of the analytical results lies in the relative rather than the absolute values.

Reductive Coupling of Peroxides in Cyclopentanol Oxidation Product.—To 15 ml. of product from the photo-catalyzed oxidation of cyclopentanol containing by analysis

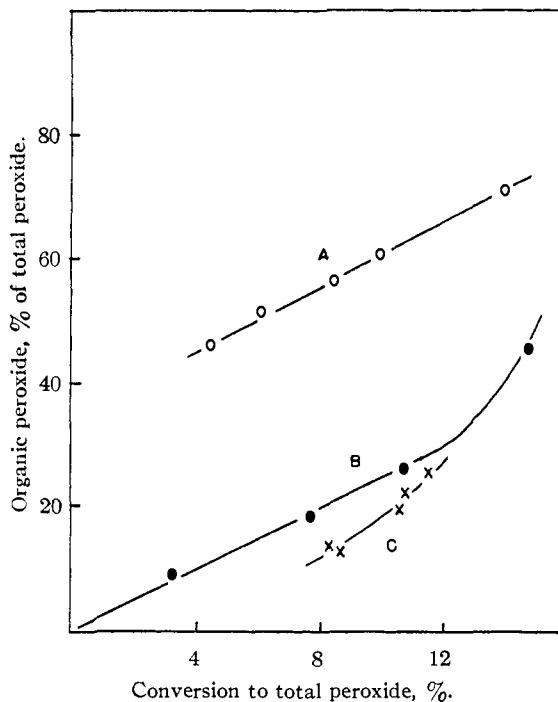


Fig. 1.—Peroxide composition vs. conversion in oxidation of cyclic alcohols; A, cyclohexanol 125° autocat. and 100° photo-init.; B, cyclopentanol 60° photo-init.; C, cyclopentanol 100° photo-init.

16.30 millimoles of peroxidic oxygen (of which 22% was "organic peroxide") was added 15.0 ml. of cyclopentanone containing 0.026 g. of sulfuric acid. The mixture was allowed to stand overnight at room temperature then analyzed as 14.80 millimoles of peroxidic oxygen, of which 76% was "organic peroxide." It was then blown with nitrogen for two hours and added under nitrogen at room temperature to a solution of 6.80 g. of ferrous sulfate heptahydrate (24.45 millimoles) in 110 ml. of deaerated methanol. From the product was isolated by the usual technique 0.421 g. crude acid, neut. equiv. 120.2 (1.75 millimoles or 23.6% yield, based on peroxide charged to coupling). The crude acid was decolorized with charcoal and recrystallized twice from water, m.p. 134°, mixed m.p. with an authentic sample of sebacic acid undepressed. Identity was confirmed by X-ray and infrared analysis.

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(5) L. C. Craig and O. Post. *Anal. Chem.*, **21**, 500 (1949).