

then allowed to pass through the solution until the exit gases gave no test for ozone. The peroxide content of the solution was then determined and found to consist of 40 mmoles of active oxygen.

For the determination of glyoxal the following procedure was used. To 1 cc. of the ozonized cyclooctatetraene solution (measured at room temp.) was added 10 cc. of water containing 1 g. of sodium bisulfite and the mixture was treated with excess 2,4-dinitrophenylhydrazine reagent and heated on the water bath for 0.5 hr. From this was obtained 0.1142 g. of glyoxal bis-2,4-dinitrophenylhydrazone, m.p. 316° (from pyridine) alone and when mixed with an authentic sample. Jacobs and Witcher¹¹ report m.p. 311-312° for this derivative. No other carbonyl products were isolated. Therefore the total yield of glyoxal from this experiment corresponds to 2.2 mmoles of glyoxal per mmole of cyclooctatetraene ozonized.

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(11) T. L. Jacobs and W. J. Witcher, *J. Am. Chem. Soc.*, **64**, 2635 (1942).

Polymethylol¹

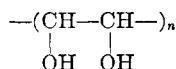
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The preparation of vinylene carbonate has been described as well as its polymerization product.² This same reference describes a hydrolysis product of the polymer as being water-soluble, and the statement is made that it is "undoubtedly $-(CH-OH)_n-$ ".³

This solubility behavior is inconsistent with the behavior of other polymeric materials having a regularly repeating sequence of hydroxyl functions along a long carbon chain. Pure poly(vinyl alcohol) of reasonably high molecular weight, for instance, is not soluble in cold water but is soluble in hot water. The solution on cooling is metastable, tending to gel on prolonged standing.

We have hydrolyzed poly(vinylene carbonate) under alkaline conditions to give a product whose solubility behavior is in line with that predicted for a polymer having the structure given.



(1) Communication No. 1916 from the Kodak Research Laboratories.

(2) M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).

(3) Since the manuscript was submitted, a paper on the hydrolysis of polyvinylene carbonate, by K. Hayashi and G. Smets, has appeared in *J. Polymer Sci.*, **27**, 281 (1958).

The carbonate was prepared by the method of Newman and Addor.² The monomer was polymerized in a sealed tube at 75°, with 0.5% of benzoyl peroxide as catalyst. The hard, clear polymer was dissolved in dimethylformamide and the solution poured into a large volume of distilled water. The white precipitate was washed with distilled water and dried at 50°. The inherent viscosity determined in dimethylformamide was 0.31. The poly(vinylene carbonate) was suspended in 1*N* sodium hydroxide solution at room temperature, the polymer soon going into solution, and the hydrolyzed product precipitating out as a white powder about a minute later. This was filtered off, washed well with water, and dried.

Anal. Calcd. for CH₂O:C, 40.0; H, 6.7. Found: C, 39.2; H, 7.2.

The filtrate obtained after hydrolysis on acidification generated carbon dioxide.

Polymethylol is insoluble in water up to 140° and in most organic solvents, swells in boiling dimethylformamide, and is soluble in hot dimethyl sulfoxide, precipitating from this hot solution on cooling. A number of derivatives could be prepared by reaction in hot dimethyl sulfoxide, including the acetate, cinnamate, and phenyl urethane.

A possible explanation for the inconsistency regarding solubility may be found in the fact that partially esterified poly(vinyl alcohol) and cellulose are water-soluble (or at least more hydrophilic), whereas the parent alcohols are insoluble in cold water. By analogy, it could be argued that the hydrolysis product obtained by Newman and Addor might have been an incompletely hydrolyzed poly(vinylene carbonate).

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A Convenient Synthesis of Glutaconic Ester

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Glutaconic ester has frequently been prepared²⁻⁴ by procedures which employ acetonedicarboxylic ester, a compound which is cumbersome to prepare but which has recently become commercially available.⁵ In the most recent procedure,³ a good yield (67%) of glutaconic ester was reported. However, the yields were variable since the required high pressure catalytic hydrogenation of acetonedicarboxylic ester was difficult to reproduce; the hydrogenation was sensitive to the age of the catalyst and to its method of preparation.

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(2) H. v. Peckmann and K. Jenisch, *Ber.*, **24**, 3250 (1891).

(3) H. L. Lochte and P. L. Pickard, *J. Am. Chem. Soc.*, **68**, 721 (1946).

(4) C. Grundmann and H. Paul, *Chem. Ber.*, **86**, 186 (1953).

(5) Available from Chas. Pfizer Co., Brooklyn, N. Y.