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Photoreductive Formation Of Acetaldehyde From Aqueous Formaldehyde

Alan W. Schwartz* and R.M. de Graaf
Evolutionary Biology Research Group,
Faculty of Science, University of Nijmegen,
Toernooiveld 1, 6525 ED, Nijmegen, The Netherlands

Abstract: A novel reaction is described in which acetaldehyde is formed by ultraviolet irradiation of mildly basic formaldehyde solutions. In 0.05 M potassium carbonate, the acetaldehyde produced is converted to pentaerythritol in a subsequent dark reaction.

The selective synthesis of pentaerythritol by ultraviolet irradiation of aqueous formaldehyde in the presence of an inorganic base has been reported.[1-2] In a typical reaction, a solution containing 0.1 M freshly distilled formaldehyde and 0.05 M K_2CO_3 was degassed with Argon and irradiated with a low pressure Mercury arc lamp (Hanovia) for 10 h at 20°C. Upon standing in the dark the irradiated solution was shown to produce increasing amounts of pentaerythritol during one or two weeks at 25°C. The maximum yield corresponded to 25% or more of the starting formaldehyde.[2]

The synthesis of pentaerythritol under these conditions suggested the possibility that acetaldehyde was being formed as precursor. Sequential aldol condensations of acetaldehyde with formaldehyde followed by a cross-Cannizzaro reaction might therefore account for the synthesis. Capillary gas chromatography of formaldehyde solutions immediately after irradiation showed the presence of a peak corresponding to acetaldehyde. The identification of acetaldehyde was confirmed by GC-MS. The concentration of acetaldehyde produced after 10 h of irradiation was found to reach 6 mM. When the fused quartz lamp housing was replaced with Vycor 791 to screen out 185 nm radiation, no acetaldehyde was detectable and the formaldehyde decomposition decreased from 51 to 3.5%.

Acetaldehyde has not previously been identified as a product of the photolysis of aqueous formaldehyde, although it has been reported among the products produced in the irradiation at 185 nm of mixtures of carbon monoxide and water vapor.[3-4]

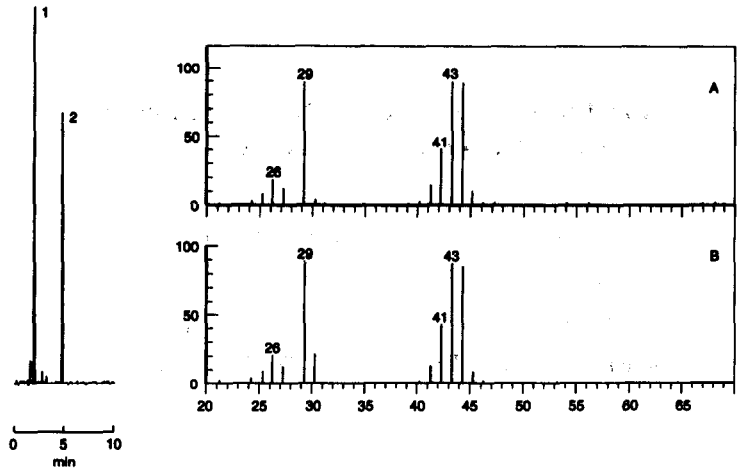

Fig. 1. Identification of acetaldehyde in an irradiated formaldehyde solution. Left: Capillary GC on CP-Wax-57 CB (Chrompack, 0.2 μm x 25m), 40°C to 80°C at 4°C/min. FID, $4x10^{-12}$. Peak 1 is acetaldehyde, peak 2 is 1-propanol (internal standard). Right: Mass spectrum of peak 1 (70 eV, corrected by subtraction of background). A, the irradiated solution. B, acetaldehyde standard.

Glyoxal, malonaldehyde, and formic and oxalic acids have been identified in formaldehyde solutions irradiated at 185 and 254 nm.[5-6]

The quantum yield for the decomposition of formaldehyde at 185 nm has been reported to approach 0.8 at 0.01 M.[6] The formation of 6 mM acetaldehyde under our conditions represents 24% of the formaldehyde which is consumed during the irradiation, suggesting a surprisingly high quantum yield for the process. We are investigating the mechanism of acetaldehyde production in more detail.

References:

1. Shigemasa, Y.; Matsuda, Y.; Sakazawa, C.; Matsuura, T. *Bull. Chem. Soc. Jpn.* **1977**, 50, 222-226.
2. Schwartz, A.W.; Graaf, R.M. de *J. Mol. Evol.* **1993**, in press.
3. Bar-Nun, A.; Hartman, H. *Origins of Life* **1978**, 9, 93-101.
4. Bar-Nun, A.; Chang, S. *J. Geophys. Res.* **1983**, 88, 6662-6672.
5. Halmann, M.; Bloch, S. *BioSystems* **1979**, 11, 227-232.
6. Park, H-R.; Getoff, N. *J. Photochem. Photobiol.* **1988**, 43, 155-163.

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