Tetrahedron Letters No. 9, pp 653 - 654, 1973. Pergamon Press. Printed in Great Britain.

FRAGMENTATION OF RADICALS DERIVED FROM GLYCOLALDEHYDE AND GLYCERALDEHYDE IN AQUEOUS SOLUTION. AN EPR STUDY.

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(Received in UK 6 December 1972; received in UK for publication 17 January 1973)

When a neutral aqueous solution of acetone and ethylene glycol is irradiated with UV-light within the cavity of an epr-spectrometer the radicals $\underline{1}$ and $\underline{2}$ are the only paramagnetic species to be observed[1]:

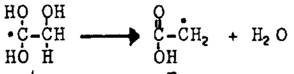
$$(CH_3)_2CO^* + HOCH_2CH_2OH \longrightarrow \underset{\underline{1}}{(CH_3)_2\dot{C}OH} + \underset{\underline{2}}{HOCH_2\dot{C}HOH} \qquad (1)$$

In strongly acidic solution, however, $\underline{2}$ eliminates a molecule of water to yield the formylmethyl radical $\underline{3}$ which can be identified by epr-spectroscopy[1,2]:

$$\underset{\underline{2}}{HOCH_2\dot{C}HOH} \xrightarrow{H^+} \underset{\underline{3}}{H_2\dot{C}CHO} + H_2O \qquad (2)$$

According to pulse radiolysis studies, this elimination is also catalyzed by OH^- [3,4].

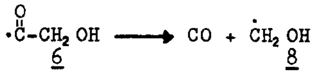
We now wish to report results obtained by irradiating o.o8 M aqueous solutions of glycolaldehyde and glyceraldehyde, respectively, containing o.8 M acetone at room temperature. If electronically excited acetone abstracts an H-atom from glycolaldehyde, which is hydrated to about 85% in aqueous solution[5], the radicals $(HO)_2\dot{C}CH_2OH$, $\underline{4}$; $HC(OH)_2\dot{C}HOH$, $\underline{5}$; $HOCH_2\dot{C}O$, $\underline{6}$, and $\underline{1}$ are expected to be formed. With the exception of $\underline{1}$, however, these radicals could not be detected between pH o and 12. Instead, the carboxymethyl radical $\underline{7}$ (a_α=21.2 Gauss) and the hydroxymethyl radical $\underline{8}$ (a_α=17.7, a_{OH}=1.o Gauss) were identified. In addition, carbon monoxide was found to be present in irradiated solutions. We suggest that $\underline{7}$ is produced from $\underline{4}$ by a 1.2-elimination of H_2O analogous to (2):



$$\underset{\underline{4}}{\cdot C(OH)_2{-}CH(OH)H} \longrightarrow \underset{\underline{7}}{HO{-}C(=O){-}\dot{C}H_2} + H_2O \qquad (3)$$

Apparently, this reaction is much faster than (2) even at neutral pH-values. As a consequence the stationary concentration of $\underline{4}$ stays below the detection limit. We suggest the heat of formation of the carboxyl group to be the driving force of reaction (3).

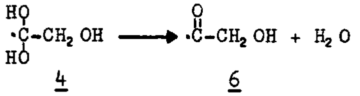
Since neither $\underline{5}$ nor radicals derived from its decomposition could be observed its formation must be of minor importance. This conclusion is in agreement with the results of Hudson[6] who found that H-atoms are more easily abstracted from acetal C-atoms than from ether C-atoms. $\underline{8}$ and CO are the products of a C-C fragmentation reaction. They are probably produced from the common precursor $\underline{6}$:



$$\cdot\overset{\overset{O}{\|}}{C}\text{-}CH_2OH \longrightarrow CO + \dot{C}H_2OH \qquad (4)$$

$$\underline{6} \qquad\qquad\qquad\qquad \underline{8}$$

In contrast to $CH_3\dot{C}O$, 6 apparently decarbonylates with high yield. This may be related to the fact that 8 is a more stable radical than $\dot{C}H_3$ [7]. Alternatively, the transition state for the fragmentation of 6 may be lowered by an interaction between the OH and CO groups. In principle, 6 can also be formed from 4 by a 1.1-elimination of water:



$$\underset{HO}{\overset{HO}{\cdot C}}\text{-}CH_2OH \longrightarrow \cdot\overset{\overset{O}{\|}}{C}\text{-}CH_2OH + H_2O \qquad (5)$$

$$\underline{4} \qquad\qquad\qquad\qquad \underline{6}$$

The question as to what extent this reaction contributes to the production of 6 is presently under investigation.

The relative concentrations of 7 and 8 depend on the pH and on the temperature of the solution. Below pH 1 and above pH lo the formation of 7 is favored with respect to that of 8. 8 seems to profit more than 7 from a temperature increase. This is in agreement with the well-known temperature dependence of decarbonylation reactions[8,9].

If glycolaldehyde is substituted by glyceraldehyde under the conditions described, the radical $HOCH_2\dot{C}HCO_2H$ (a_α=2o.5, a_β=28.o, a_{OH}=o.25 Gauss)[1o], which results from $(HO)_2\dot{C}CH(OH)CH_2OH$ by a 1.2-elimination of water analogous to (3), and the radical $HO\dot{C}HCH_2OH$ (a_α=18.2, a_β=9.1, a_{OH}=1.2, $a_{OH'}$=o.2 Gauss), which is the product of a C-C fragmentation reaction analogous to (4), can be identified. As with glycolaldehyde, carbon monoxide is found as a reaction product.

If H-atoms are abstracted from glycolaldehyde or glyceraldehyde by $\dot{O}H$-radicals generated by gamma-irradiation of aqueous solutions, CO can also be detected. This result excludes a decarbonylation mechanism by which CO is exclusively formed by direct fragmentation of the electronically excited carbonyl compounds as was observed for dibenzylketone by Quinkert[11].

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