THE PHOTOLYSIS OF TRIOSES IN AQUEOUS SOLUTION

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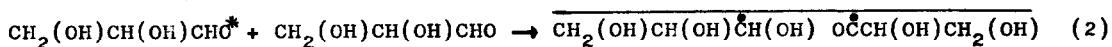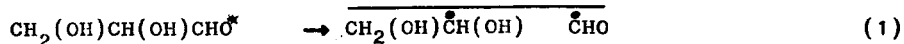
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The photochemical behaviour of carbohydrates is not known in most cases. Recently, the photochemistry of the simplest of all sugars, namely glycolaldehyde, has been investigated and it could be shown, that this compound cleaves from an excited triplet state into a formyl and an hydroxy methyl radical [1]. In this work the photochemistry of glyceraldehyde (I) and 1,3-dihydroxyacetone (II) are reported. The phosphate esters of both compounds are of significant importance in biochemistry and therefore their photochemical behaviour is of a considerable interest.

Both compounds have been photolyzed in aqueous solution (D_2O) inside the probe of a Varian A 60 nmr spectrometer with a high-pressure mercury lamp. The reaction products were identified by the "Chemically Induced Dynamic Nuclear Polarization" (CIDNP) method [2]. The nmr spectra of both trioses are rather complex, because they are in equilibria with dimeric forms and their hydrates [3].

Upon irradiation of I two emission signals at $\delta = 4.5$ and $\delta = 9.7$ ppm are observed (fig.1), which are due to the starting material in its unhydrated monomeric form. It is impossible to deduce from this spectrum whether the aldehyde undergoes α-cleavage or photoreduction with itself, because both processes would lead to polarized starting material, which may be formed via step (1) or (2) by either recombination or disproportionation, respectively.

$$CH_2(OH)CH(OH)CHO^* \longrightarrow \overline{CH_2(OH)\overset{\bullet}{C}H(OH) \quad \overset{\bullet}{C}HO} \tag{1}$$

$$CH_2(OH)CH(OH)CHO^* + CH_2(OH)CH(OH)CHO \longrightarrow \overline{CH_2(OH)CH(OH)\overset{\bullet}{C}H(OH) \quad \overset{\bullet}{O}CCH(OH)CH_2(OH)} \tag{2}$$

To decide which reaction occurs the following reasoning was applied: If I clea-
ves into a 1,2-dihydroxyethyl and a formyl radical, it should be possible to
trap the latter radical. Indeed, after adding some drops of carbon tetrachloride
to the aqueous solution, polarized chloral hydrate is observed in emission. Chlo·
ral hydrate can only be formed by a random combination of a trichloromethyl and
a formyl radical. The generated chloral is then immediately hydrated and the po-
larization is observed in its hydrate. This experiment proves that during photo-
lysis of I the formyl radical is generated. With the known g-values of both ra-
dicals[4,5] and applying the rules of CIDNP [6], the spectrum is explained by an α-
cleavage from an excited triplet state into a radical pair, which recombines to
the starting material. The weak polarization of the aldehyde proton suggests
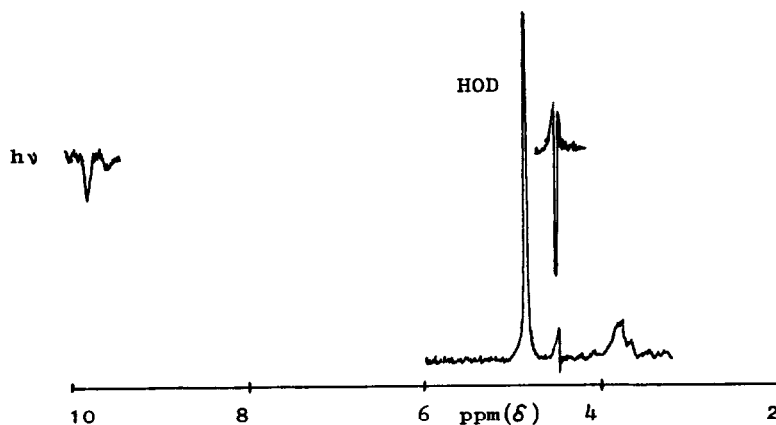however, that α-cleavage is not the dominant process, since the CIDNP signal

Fig.1: The nmr spectrum of I. Upper trace: CIDNP signals during photolysis

should be stronger because of the large hyperfine coupling constant of the for-
myl radical. The CIDNP experiment only shows that α-cleavage occurs to a certain
extent. In the presence of carbon tetrachloride other polarized products are
chloroform and formic acid.

The photolysis of II is easier to understand. The nmr signal of the monomeric form turns into emission during irradiation (fig.2). This CIDNP signal can only be explained by an α-cleavage from an excited triplet state of the ketone into an hydroxyacetyl and an hydroxymethyl radical as shown below

$$CH_2(OH)COCH_2(OH) \longrightarrow \overline{CH_2(OH)\overset{\bullet}{C}O \quad \overset{\bullet}{C}H_2(OH)}$$
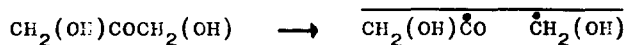
The g-value of the hydroxyacetyl radical should be in the same order of magnitude as the g-value of the acetyl radical (2.0005) [7], while the g-value of the hydroxymethyl radical has been measured to be 2.0033 [5]. This difference of the g-values causes the observed energy polarization after the radicals have recombined to the starting material. The radical pair does not disproportionate into glycolaldehyde and formaldehyde, otherwise a CIDNP signal between δ = 9 and 10 ppm would appear. This disproportionation reaction is often observed during photolysis of α-hydroxy keto compounds, for example with 3-methyl-3-hydroxy-2-butanone, where α-cleavage is followed by disproportionation into acetone and acetaldehyde [8,9].
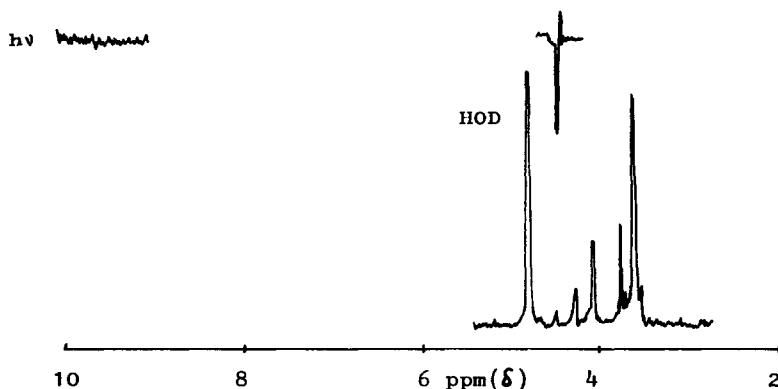

Fig.2: The nmr spectrum of II. Upper trace: CIDNP signal during photolysis

Although both compounds hardly posess chromophoric groups, because they are largely dimerized and hydrated in aqueous solution, they still undergo photochemical reactions. Assuming a small quantum yield, which is demonstrated by the polarized starting material, then the CIDNP spectroscopy seems to be the only

method for investigating the photochemistry of these simple carbohydrates. Tetroses and pentoses do not show any CIDNP signals during photolysis.

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REFERENCES:

1.   K.G.Seifert and J.Bargon, Angew.Chem. 85, 768 (1973).

2.   G.L.Closs, Proc.Int.Congr.Pure Appl.Chem.,XXIIIrd Spec.Lect. 4,19 (1971).

3.   E.F.H.Brittain, W.O.George and C.S.Collins, J.Chem.Soc. (B) 1971, 2414.

4.   F.J.Adrian, E.L.Cochran and V.A.Bowens, J.Chem.Phys. 36, 1661 (1962).

5.   R.Livingston and R.Zeldes, J.Chem.Phys. 44, 1245 (1966).

6.   R.Kaptein, J.Amer.Chem.Soc. 94, 6251 (1972).

7.   J.E.Bennet and B.Mile, Trans.Farad.Soc. 67, 1587 (1971).

8.   G.P.Laroff and H.Fischer, Hel.Chim.Acta 56, 2011 (1973).

9.   J.Bargon and K.G.Seifert, Ber.Bunsenges.Phys.Chem. 78,187 '1974).