

ENOL INTERMEDIATES IN PHOTOREDUCTION AND TYPE I CLEAVAGE REACTIONS OF ALIPHATIC ALDEHYDES AND KETONES†

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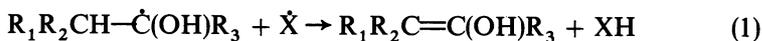
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ABSTRACT

Several unstable simple enols including ethenol (vinyl alcohol) and 2-propenol (the enol of acetone) are observed by CIDNP spectroscopy during photoreduction of aliphatic aldehydes and ketones and Type I cleavage of α -hydroxyketones. They are formed by disproportionation reactions of α -hydroxy alkyl radicals and tautomerize to the stable keto forms. The NMR parameters of the enols are discussed. For the 2-propanol-acetone system deuterium substitution reveals the relative rate constants of disproportionation and combination of the 1-hydroxy-1-methylethyl radical.

1. INTRODUCTION

The formation of transient enols is a well known step in the Type II elimination of alkanones with γ -hydrogen atoms and in related reactions^{1, 2}. Recently, it has been shown by several authors³⁻⁶ that enols are also formed by disproportionation of α -hydroxy alkyl radicals bearing at least one β -hydrogen atom (1) and generated in photoreduction reactions of ketones



and aldehydes and in the course of Type I cleavage of α -hydroxyketones in solution. Reaction (1) has been mentioned before⁷; however, its relevance with respect to the photochemical reaction mechanisms of ketones and aldehydes has not been discussed extensively⁸.

In this paper we present an extension of our previous studies^{4, 5} and report on the formation of ethenol (vinyl alcohol) during photoreduction of acetaldehyde and during cleavage of 3-hydroxy-2-butanone, of 1-propen-1-ol, 1-buten-1-ol and 3-methyl-1-buten-1-ol during photoreduction of propionaldehyde, butyraldehyde and 3-methyl-butyraldehyde, of 2-propenol (the enol of acetone) during photoreduction of acetone and cleavage of 3-hydroxy-3-methyl-2-butanone, and of 2-pentene-3-ol during cleavage of 3-hydroxy-3-ethyl-2-pentanone. The species are detected by n.m.r. spectroscopy during

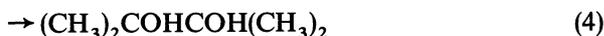
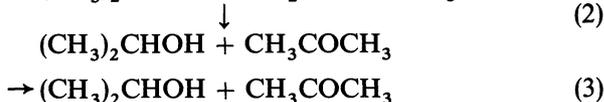
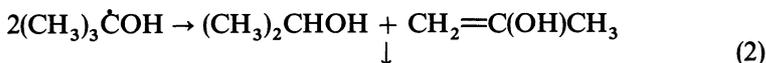
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the photochemical reactions in solution and are easily observed since they exhibit large chemically induced dynamic nuclear polarizations (CIDNP)⁹. From the CIDNP effects and the yields of the various reaction products the radical reaction mechanisms are derived. For several systems they are supported by direct e.s.r. observation of the intermediate radicals.

One particular system, the photoreduction of acetone with 2-propanol¹⁰ is considered in detail. It is shown that the enol formation via reaction (2), i.e. CH-disproportionation, is favoured over terminations by OH-disproportionation (3) and combination (4). Reformation of ketone via an enol



intermediate is thus an effective pathway of ketone deactivation.

2. EXPERIMENTAL AND ANALYSIS

Carbonyl compounds and solvents were obtained from FLUKA in the purest available form and used without further purification. 3-Pentanone was freshly distilled before use. 3-Hydroxy-3-ethyl-2-pentanone was prepared by the method of Hennion and Watson¹¹. For the experiments on quantitative product analysis in the acetone-2-propanol system (Section 4 below) 2-propanol was distilled over sodium and all reagents were kept over molecular sieves. The solutions were freed from dissolved oxygen by several freeze-thaw cycles and sealed before use.

The e.s.r. spectra of transient radicals were obtained at $(26 \pm 3)^\circ\text{C}$ with an arrangement described earlier¹². For the CIDNP experiments, dilute solutions of the aldehydes and ketones in benzene, acetonitrile- d_3 or octamethylcyclotetrasiloxane (OMCTS) were irradiated in the $n\pi^*$ -transition region at $(26 \pm 3)^\circ\text{C}$ within a modified probe of an n.m.r. spectrometer¹³. In product analysis of n.m.r. (Section 4) integrals were obtained by weighing peak area cut-offs from photocopies. Absolute concentrations were determined by comparing integrals with the integral of a known concentration of the internal standard acetonitrile.

Experimental enhancement factors of the CIDNP effects were determined by the previously described procedure¹³. The effects were analysed in terms of the high-field radical pair theory^{9, 14} both qualitatively and quantitatively with the aid of computer simulations¹³. Relative rates of formation of two pair products of the same radical pair result from the CIDNP intensities of equivalent transitions of the two products via

$$f_1/f_2 = I_1/I_2 \times T_{12}/T_{11} \quad (5)$$

where T_{11} and T_{12} are the longitudinal relaxation times of the two products¹⁵.

In the following, several cases will be presented where one product may be formed from two different radical pairs, $\overline{\text{R}}_a \cdot \cdot \text{R}_b$ and $\overline{\text{R}}_b \cdot \cdot \text{R}_a$, respectively.

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Best fits of calculated to experimental CIDNP effects of this product were obtained by superposition of spectra calculated for product formation from $\overline{R}_a \cdot \overline{R}_b$ and $\overline{R}_b \cdot \overline{R}_b$ only. The individual spectra were computed for pair formation rates of unity, equal diffusion parameters and reaction constants $\lambda^{13, 14}$. The relative contributions giving the best fit do not in general represent the relative rates of formation of the pairs (*vide infra*).

3. CIDNP EFFECTS AND REACTION MECHANISMS

3.1. Acetaldehyde and 3-hydroxy-2-butanone, ethanol

During irradiation of 0.2M acetaldehyde or 0.2M 3-hydroxy-2-butanone the CIDNP effects of *Figure 1* are obtained⁴. The same effects are observed

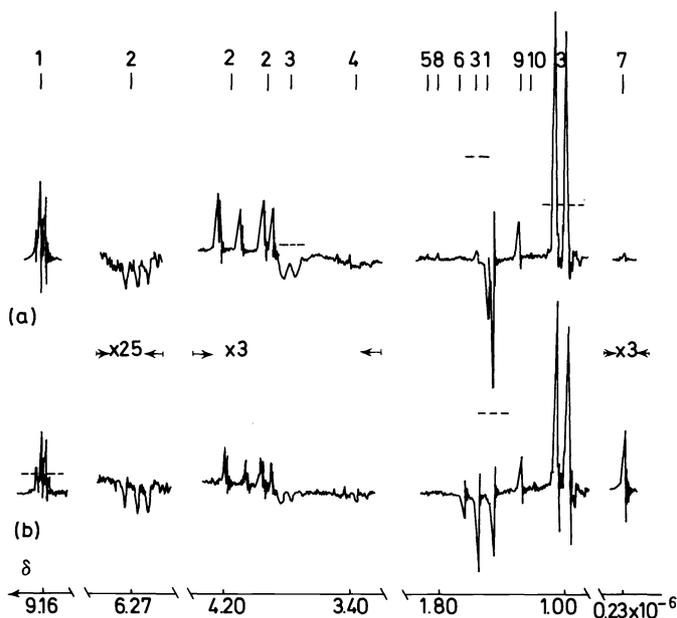


Figure 1. CIDNP during photolysis of 3-hydroxy-2-butanone (a) and acetaldehyde (b) in benzene. Parts of spectrum at enhanced sensitivity. ---: line intensities before photolysis. Assignment of transitions, see *Table 1*.

for cyclohexane and OMCTS solvent. *Table 1* shows the assignment of the transitions 1–10 of *Figure 1* to the various reaction products based on comparison of chemical shifts with those of authentic compounds, and gives the product yields. The similarity of the CIDNP effects and the product distribution indicates that for both systems the same primary radical reactions occur. This is supported by the e.s.r. observation of the 1-hydroxyethyl radical $\text{HO}\dot{\text{C}}\text{HCH}_3$ during photolysis of acetaldehyde and 3-hydroxy-2-butanone in solution¹⁶. Furthermore acetaldehyde is a major product of photoreactions of 3-hydroxy-2-butanone¹⁷ and the hydroxyketone is formed during u.v. irradiation of acetaldehyde in solution¹⁸.

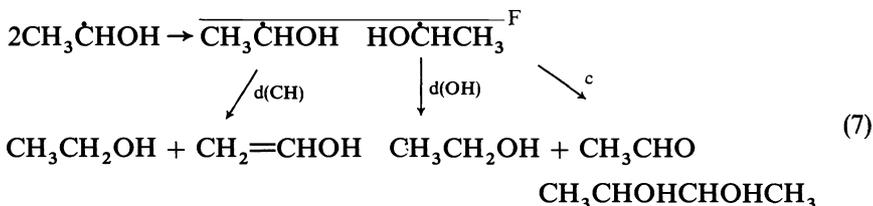
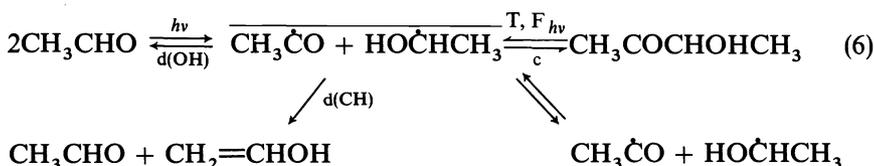
Table 1. Assignment of products and product yields for the photoreactions of 0.2 M acetaldehyde and 0.2 M 3-hydroxy-2-butanone in benzene

| Transition | Product | yield† | yield‡ |
|------------|---------------------------------------|--------|--------|
| 1 | CH ₃ CHO | — | 34.1 |
| 2 | CH ₂ =CHOH | — | — |
| 3 | CH ₃ COCHOHCH ₃ | 31.0 | — |
| 4 | CH ₃ CH ₂ OH | 13.3 | 24.1 |
| 5 | CH ₃ COCOCH ₃ | 0.8 | 0.9 |
| 6 | CH ₃ COCH ₃ | 3.5 | <0.2 |
| 7 | CH ₄ | 3.0 | <0.2 |
| 8–10 | unassigned | 22.1 | 15.6 |

† Acetaldehyde photolysis, in per cent of reacted acetaldehyde after 90 sec irradiation, conversion 20 per cent.

‡ 3-Hydroxy-2-butanone photolysis, in per cent of reacted ketone after 90 sec irradiation, conversion 22 per cent.

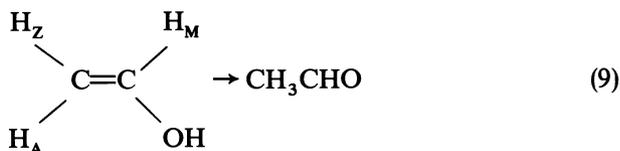
To explain the observations, we suggest the radical reactions of *Scheme 1*.

Scheme 1

Decarbonylation of the acetyl radicals leads to further secondary radical reactions as is evident from the reaction products (*Table 1*). In the scheme c, d(OH) and d(CH) indicate the pair reactions combination, disproportionation by OH- and CH-hydrogen transfer, respectively. The labels T and F give the modes of pair formation. The acetyl-1-hydroxyethyl radical pairs may be formed by reactions of excited triplet state with ground state acetaldehyde or by Type I cleavage of triplet hydroxy-ketone (T) or by diffusive encounters of spin uncorrelated radicals (F) whereas the latter mode (F) is the only one for the symmetric pair in reaction (7). It can be shown easily that these modes combined with the reactions of *Scheme 1* and the known magnetic properties^{12, 16} of the radicals explain all the observed CIDNP effects of *Figure 1*.

The formation of ethenol (vinyl alcohol) in reactions (6) and (7) is postulated for several reasons. First, CH-disproportionation in reaction (6) easily

explains the enhanced absorption of the CHO-proton of acetaldehyde. Secondly, the olefinic transitions labelled 2 in *Figure 1* require the formation of an olefinic product. Their positions are best explained by an olefinic AMZ-system with $\delta_A = 4.13$, $\delta_M = 6.27$ and $\delta_Z = 3.91$ p.p.m., $|J_{AM}| = 14.0$, $|J_{AZ}| = 1.8$ and $|J_{MZ}| = 6.5$ Hz, indicating substitution by an OR-group^{19, 20}. The product must be unstable since no product resonances are found even after long irradiation time, and, further, traces of acid quench the appearance of the olefinic resonances. The formation of ethenol is in complete accord with these findings since this compound will tautomerize to acetaldehyde, the rate increasing with acid concentration.



After irradiation, the enhanced absorption of H_A at 4.20 p.p.m. (*Figure 1*) decays by a first order rate law with a rate constant $k = 0.102 \text{ s}^{-1}$. This is related to the lifetime τ of ethenol by

$$k = \tau^{-1} + T_1^{-1} \quad (10)$$

where T_1 is the longitudinal relaxation time of the transition. Assuming $T_1 = 16 \text{ s}$ as found for the corresponding transition of vinyl ethyl ether in the same solvent, τ is estimated to be 25.5 s. This estimate gives an order of magnitude only, but from equation (10) $\tau > k^{-1} \approx 10 \text{ s}$ is clearly evident. We believe that our estimate gives a lower limit for the uncatalysed reaction (9) since acid impurities might be present.

The reactions of *Scheme 1* are further supported by computer simulations of the ethenol CIDNP effects. In *Figure 2* we show the results of calculations for the vinyl protons. The OH-proton resonance is not included since it shows only very small effects. The calculations are based on the known g -factors and coupling constants^{12, 16} of the radicals with $a_H > 0$ for $\text{CH}_3\dot{\text{C}}\text{O}$, and $a_\alpha^H < 0$ and $a_\beta^H > 0$ for $\text{HO}\dot{\text{C}}\text{HCH}_3$, the n.m.r.-parameters given above for ethenol, and $J_{AM} > 0$, $J_{AZ} < 0$, $J_{MZ} > 0$ as for related compounds¹⁹. *Figure 2(a)* shows a spectrum calculated for reaction (6) [d(CH), pure T-pair formation], *Figure 2(b)* shows a spectrum for reaction (7) [d(CH), pure F-pair formation]. The two spectra are scaled to give comparable maximum amplitudes. A best fit to the experimental spectrum [*Figure 2(c)*] is a 60:40 superposition of properly scaled spectra calculated for reactions (6) and (7) with the appropriate pair parameters^{13, 14} [*Figure 2(d)*]. *Figure 2(e)* gives an experimental spectrum observed during irradiation of 0.2 M acetaldehyde in benzene- d_6 containing 1.8 M $\text{CH}_3\text{CH}_2\text{OD}$. Since in this system the photo-reduction



should occur simultaneously with reaction (6) a larger contribution of the effects of reaction (7) [*Figure 2(b)*] is expected. In fact, now the best fit is a 10:90 superposition of the effects of reactions (6) and (7).

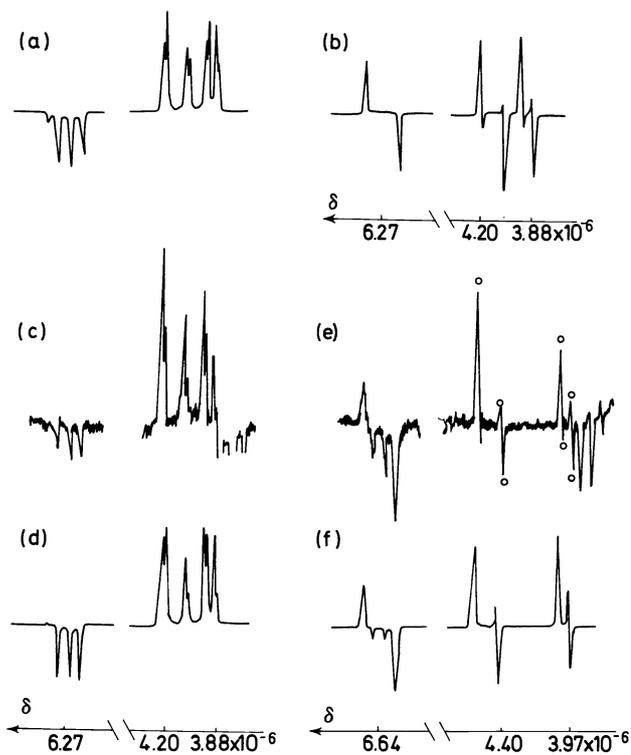


Figure 2. CIDNP patterns of the vinyl protons of ethenol. a, b, d, f: calculated, c, e: experimental, see text.

From the findings that the best fits require superpositions, the importance of both reactions (6) and (7) for enol formation is evident. However, the relative contributions of (6) and (7) cannot be obtained, because several pair formation modes (T, F and even S) and several reaction channels may exist besides those used in the calculation.

3.2. Propionaldehyde, *cis*- and *trans*-1-propen-1-ol

CIDNP effects and e.s.r.-spectra of transient radicals during photo-reactions of propionaldehyde solutions have recently been reported by Cocivera^{21, 22} *et al.* For acetonitrile solvent the authors find Type I cleavage, whereas photoreduction as for acetaldehyde (6) predominates in perfluoromethylcyclohexane. For the latter system enol formation is supposed to occur²², however, only very weak signals attributable to this species were observed and no full analysis was given.

We found that CIDNP effects very similar to those reported by Cocivera^{21, 22} for perfluoromethylcyclohexane solutions appear during irradiation of propionaldehyde in octamethylcyclotetrasiloxane (OMCTS). Figure 3(a) shows part of a spectrum obtained for a 0.5M solution. Apart from lines due to propionaldehyde (9.59 p.p.m.), *n*-propanol (3.42 p.p.m.)

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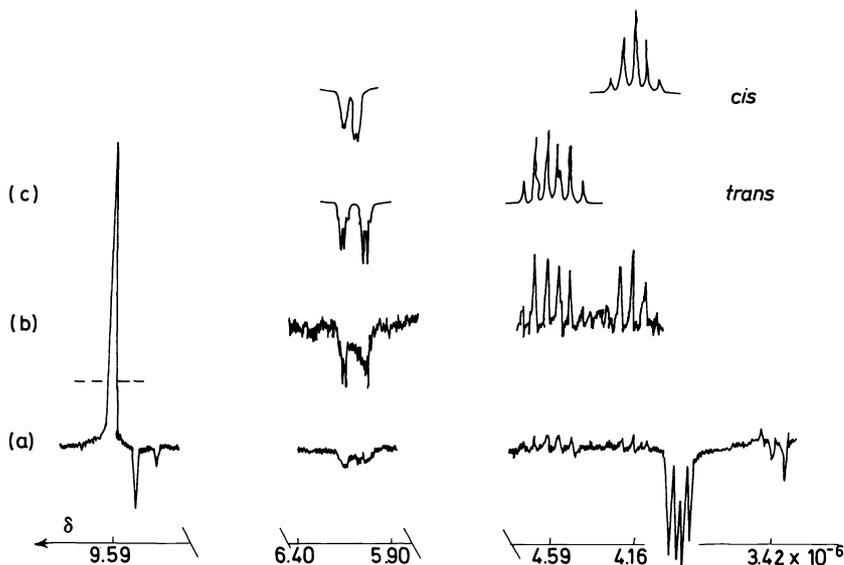
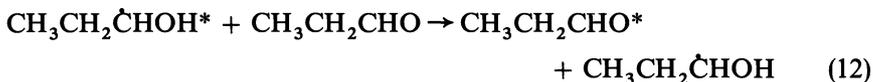
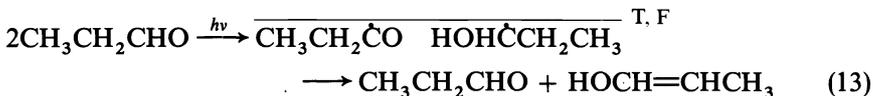


Figure 3. CIDNP during photolysis of propionaldehyde in OMCTS (a), enol resonances at enhanced sensitivity (b) and calculated (c).

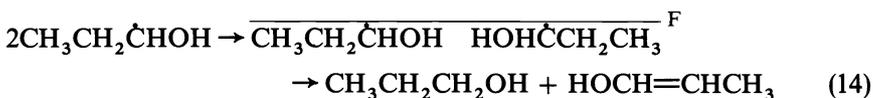
and 4-hydroxy-3-hexanone ($\delta = 3.91$ p.p.m.) olefinic transitions are now found in the range $4.00 \leq \delta \leq 6.00$ p.p.m. They are displayed with enhanced spectrometer sensitivity in Figure 3(b). The close resemblance of the CIDNP effects observed for perfluoromethylcyclohexane and OMCTS solutions indicate that photoreduction^{21, 22} also predominates for the latter solvent. Cocivera^{21, 22} has explained most of the effects in terms of reactions analogous to those formulated for acetaldehyde (6)–(8) and included the transfer reaction²³



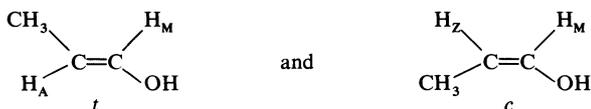
Our results support this explanation^{21, 22}. In particular, the observation of olefinic transitions confirms the formation of intermediate enols via



and



These transitions belong to unstable products, are quenchable by traces of acids and exhibit chemical shifts compatible with the structures



i.e. *trans*- and *cis*-1-propen-1-ol. Figure 3(c) shows our assignment of the alkene resonances to the *cis*- and *trans*-enols. It is based on the rules that *trans* vicinal coupling constants are larger than *cis* vicinal couplings and that *cis* allylic coupling constants are larger than the corresponding *trans* couplings²⁴. The patterns are calculated with the known e.s.r.-parameters of propionyl¹² and 1-hydroxy-1-propyl²⁵ radicals and the assumption that the radical pairs of reactions (13) (pure T-pair formation) and (14) (pure F-pair formation) each contribute about 50 per cent to the observed effects. The chemical shifts and coupling constants are given in Table 2. Obviously, a good agreement between calculated and observed CIDNP effects is obtained. Resonances of the methyl protons of the enols are not detected, presumably, because they are only little affected by nuclear polarization in the pairs.

Integration of the transitions assigned to H_A for the *trans*-enol ($\delta = 4.59$ p.p.m.) and to H_Z for the *cis*-enol ($\delta = 4.16$ p.p.m.) yields nearly equal intensities for both groups. Since these transitions arise from protons which are equivalent in the radical precursor²⁵ (HO $\dot{\text{C}}\text{HCH}_2\text{CH}_3$) equation (5) can be applied to determine the relative rates of formation of *cis*- and *trans*-enol. The relaxation times of the two species should be approximately equal, thus both enols are formed with nearly equal probabilities. This result is not unexpected regarding the rapid internal rotation in the radical at room temperature²⁵. It conflicts, however, with the analysis of an enol spectrum observed by Bargon and Seifert during the photoreaction of 1-propanol with acetone⁶.

3.3. Butyraldehyde and 3-methylbutyraldehyde, *cis*- and *trans*-1-buten-1-ol and 3-methyl-1-buten-1-ol

During irradiation of 0.5M solutions of these aldehydes in OMCTS rather complex CIDNP effects appear which have not been fully analysed. Enhanced absorption of the CHO-resonances indicate photoreduction reactions like (6), (13) or a transfer reaction (12). In regions of chemical shifts of alkene protons the transitions displayed in Figures 4(a) and 5(a) are observed. They show the typical behaviour of enol transitions, as discussed in the previous sections, and are attributed to *cis*- and *trans*-1-buten-1-ol



and to *cis*- and *trans*-3-methyl-1-buten-1-ol,



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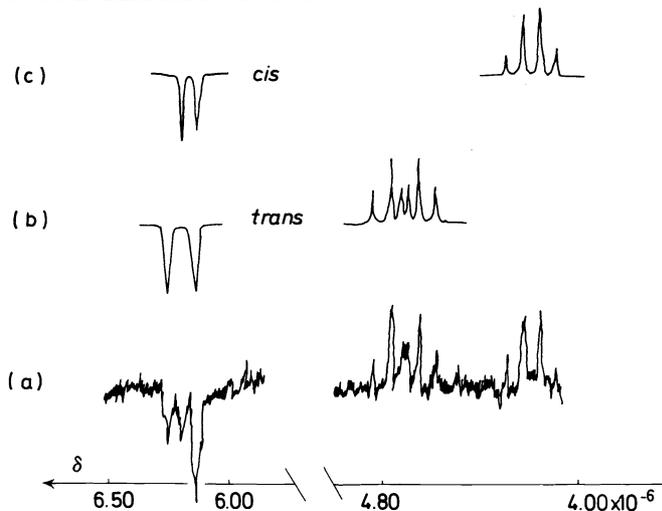


Figure 4. CIDNP pattern of 1-buten-1-ol during photolysis of butyraldehyde in OMCTS (a), calculated patterns: (b) and (c).

respectively. The reactions leading to these species are the CH-disproportionations of radical pairs $\text{R}-\text{CH}_2-\dot{\text{C}}\text{O HOHC}-\text{CH}_2-\text{R}$ and $\text{R}-\text{CH}_2-\dot{\text{C}}\text{OH HOHC}-\text{CH}_2-\text{R}$ with $\text{R} = \text{CH}_2\text{CH}_3, \text{CH}(\text{CH}_3)_2$ as formulated in sections 3.1 and 3.2 for acetaldehyde and propionaldehyde. The assignments of the transitions to the *cis*- and *trans*-enols are given in Figures 4(b), (c) and 5(b), (c). The patterns were calculated assuming the

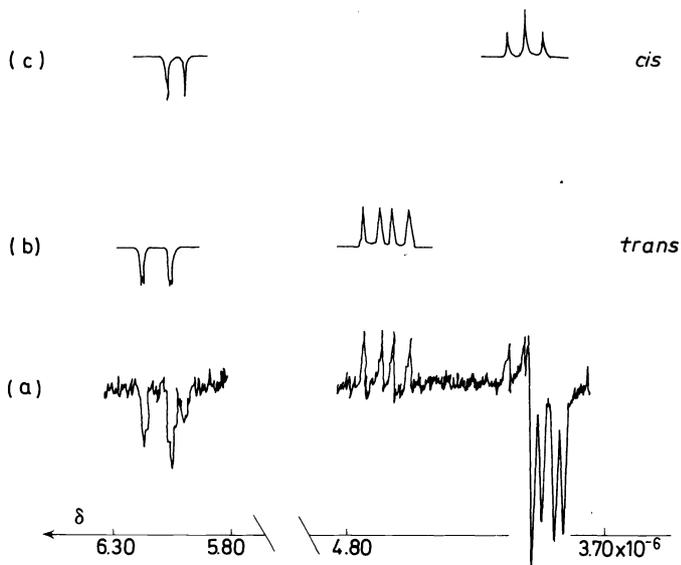


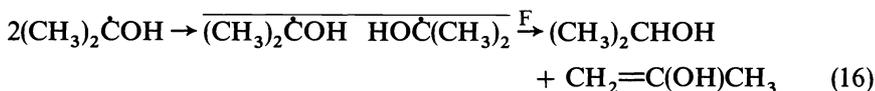
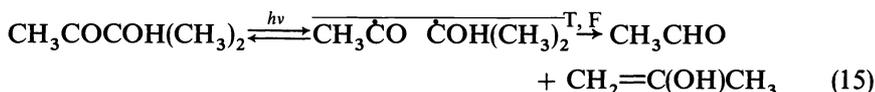
Figure 5. CIDNP pattern of 3-methyl-1-buten-1-ol during photolysis of 3-methylbutyraldehyde in OMCTS (a), calculated patterns: (b) and (c).

e.s.r.-parameters of the butyryl radicals to be equal to those of propionyl¹² and those of the 1-hydroxy-3-methylbutyl to be equal to those of the 1-hydroxybutyl radical²⁵. Further, the n.m.r.-parameters as given in *Table 2* were used, and the superposition procedure described earlier was again applied. Best fits were obtained for 70:30 and 65:35 superpositions for the two buten-1-ols. The alkyl substituents of the enols do not exhibit large CIDNP effects.

Two other aldehydes were also investigated. During irradiation of valeraldehyde which is known to undergo predominant Type II cleavage²⁶ very weak CIDNP effects attributable to the corresponding enols are observed. The low intensity did not allow any detailed analysis. 2-Methylpropionaldehyde gave rise to large CIDNP effects which were analysed in terms of Type I cleavage¹³ and did not lead to detectable enol signals.

3.4. 3-Hydroxy-3-methyl-2-butanone and acetone, 2-propenol

In an earlier paper we have shown that 2-propenol, the enol of acetone, is formed by reactions of acetyl and 1-hydroxy-1-methyl-ethyl radicals after Type I cleavage of 3-hydroxy-3-methyl-2-butanone.



Product yields and enhancement factors were given⁵ and a best fit to the experimental CIDNP spectrum of the enol was a 25:75 superposition of the effects calculated from reactions (15) (pure T-pair formation) and (16). The enol was also observed⁵ during the photoreduction of acetone with 2-propanol in acetonitrile solvent where it is formed in the sequence of reactions (2)–(4). A lifetime of 14 s was estimated using the analysis outlined in section 3.1. Comparison of this value with the reported²⁷ lifetime in the gas-phase of about 200 s indicates that the shorter lifetime in solution may be determined by acid or base impurities. Some aspects of product formation in the acetone–2-propanol system will be dealt with in section 4. The enol of acetone has also been observed by Bargon and Seifert⁶.

3.5. 3-Hydroxy-3-ethyl-2-pentanone, 2-pentene-3-ol

During irradiation of a 0.1 M solution of 3-hydroxy-3-ethyl-2-pentanone in acetonitrile-*d*₃ the CIDNP effects of *Figure 6(a)* are observed. The various transitions are assigned to the hydroxyketone (1; $\delta = 0.77$ p.p.m.: CH_2CH_3 group, emission E; $\delta = 1.74$ p.p.m.: CH_2CH_3 group, enhanced absorption A; $\delta = 2.16$ p.p.m.: CH_3CO group, E), the products acetaldehyde (3; $\delta = 2.13$ p.p.m.: CH_3 group, E; $\delta = 9.84$ p.p.m.: CHO group, A) and 3-pentanone (4; $\delta = 1.00$ p.p.m.: CH_3 group, A; $\delta = 2.43$ p.p.m.: CH_2 group, A) and to the H_Z - and H_A -protons of *trans*- and *cis*-2-pentene-3-ol (*2t*: $\delta = 4.15$ p.p.m., A; *2c*: $\delta = 4.44$ p.p.m., A). Probably because of strong overlap with other resonances the alkyl groups of the enols were not observed. Transition 5 was

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not assigned, the lines 6 belong to acetonitrile-d₂ impurities. The CIDNP-effects are efficiently quenched by 10⁻⁴ M *trans*-stilbene, an effective triplet quencher, indicating predominant triplet reaction of the excited hydroxyketone. Reactions (17) explain the phases of the CIDNP effects of the enols,

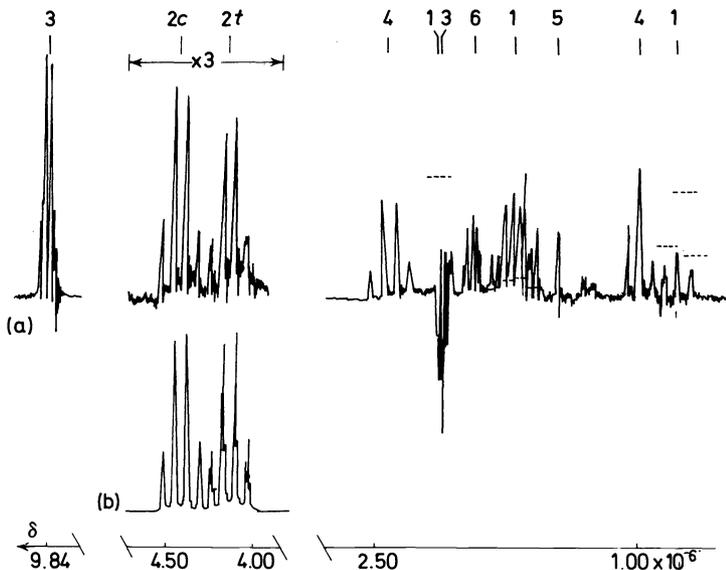
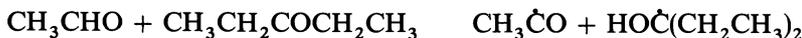
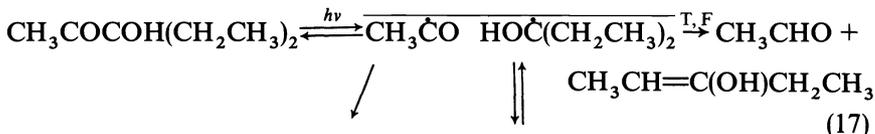


Figure 6. CIDNP during photolysis of 3-hydroxy-3-ethyl-2-pentanone in acetonitrile-d₃ (a). Parts of spectrum at enhanced sensitivity, ---: line intensities before photolysis. Assignment of transitions, see text. (b) calculated enol spectrum.

acetaldehyde and the CH₃CO and CH₂ transitions of the hydroxyketone according to the usual analysis^{9, 14} with the aid of the known e.s.r.-parameters of the intermediate radicals^{12, 13}. The emission of the CH₃CH₂-group of the hydroxyketone would be compatible with a negative sign of the coupling



constant of the CH₃-protons in the radical, though this constant should be fairly small. The enhanced absorption of the 3-pentanone CH₃ group is not

explained by reactions (17). Of the many possibilities we prefer an explanation via a secondary photoreaction of the 3-pentanone, a major product, which in a control experiment was found to lead to this enhanced absorption.



The known Type I cleavage (18) of the ketone from a triplet state^{12, 28, 29} also leads to emission for the CH₂-protons of 3-pentanone. In the photoreaction of the hydroxyketone we observed enhanced absorption for these protons [Figure 6(a)] which is explained by (17). Thus, we believe that (17) and (18) contribute to the polarizations of 3-pentanone during photolysis of 3-hydroxy-3-ethyl-2-pentanone, (17) dominating for the polarizations of the CH₂ group and (18) dominating for the CH₃ group. This view is supported by the findings that the amplitudes of the polarizations of 3-pentanone depend on hydroxyketone concentration and conversion.

As in the previously described systems of sections 3.1 to 3.4 we expect enol formation by the disproportionation of the 1-hydroxyalkyl radicals besides reaction (17). In fact, a 55:45 superposition of the effects calculated from (17)



(pure T-pair formation) and from (19) gave the best fit to the experimental spectrum of the *trans*-enol [Figure 6(b)]. For the calculation the n.m.r.-parameters given in Table 2 were used. $J_{\text{H,CH}_2} < 0$ was chosen because only this choice gave a reasonable fit. The same superposition for the *cis*-enol is also shown in Figure 6(b). Here, however, the relative intensities of the lines are independent of the ratio of superposition, because $J_{\text{H,CH}_2}$ is smaller than the linewidth, and our choice of superposition is arbitrary.

The integrals of the CIDNP transitions of *cis*- and *trans*-enols are equal. This indicates formation of both species in about equal amounts since the relaxation times of the two species can be expected to be nearly identical.

3.6. Discussion

In the previous sections it was shown that transient enols are formed by disproportionation reactions of α -hydroxyalkyl radicals after Type I cleavage of α -hydroxyketones and photoreduction of aliphatic aldehydes and ketones. The species are detected by n.m.r. because of the large signal enhancements and appear to exist for 10–20 s before tautomerization to the more stable keto form. The amount of enol formed cannot be determined directly from the CIDNP spectra. However, the stationary concentration may be estimated as follows. The intensity of the CIDNP signals I is related to the thermal equilibrium signal I_0 by^{9, 14, 20}

$$I = V \times T_1 \times \tau^{-1} \times I_0 \quad (20)$$

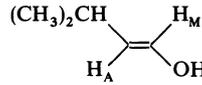
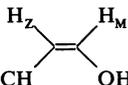
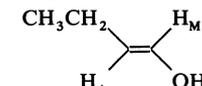
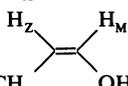
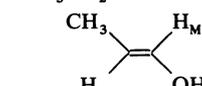
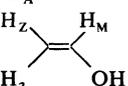
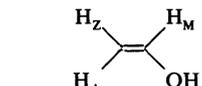
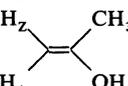
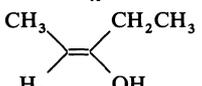
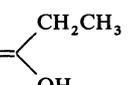
where V is the enhancement factor per product molecule, T_1 is the longitudinal relaxation time and τ the lifetime of the enol. In earlier studies^{5, 13} V was found to be about 500–2000 for reactions similar to those considered here. In the present case $T_1 \approx \tau$ (section 3.1, 3.4) thus $I \approx 10^{+3}I_0$. The observed CIDNP intensities I correspond to concentrations of about

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10^{-1} M. Thus the stationary enol concentration is of the order of 10^{-4} M. The rate of enol formation follows from this figure as $I_0 \times \tau^{-1} \approx 10^{-5}$ M sec $^{-1}$. Under our experimental conditions the rate of educt consumption was found to be about 10^{-4} M s $^{-1}$, thus the enol formation contributes about ten per cent to the overall reaction mechanism. The uncertainties of this estimate are large; however, enol formation seems to be a non-negligible pathway.

The parameters used in the calculation of the CIDNP spectra of the various enols are given in Table 2. For several cases the n.m.r. data of alkyl substituents could not be determined because of severe overlap with other polarized groups.

Table 2. Some n.m.r. and CIDNP parameters of enols†

| Enol | Solvent | $\delta_A \times 10^6$ | $\delta_M \times 10^6$ | $\delta_Z \times 10^6$ | J_{AM} | J_{AZ} | J_{MZ} | S^\ddagger |
|---|-------------------------------|------------------------|------------------------|------------------------|----------------|----------|----------|--------------|
|  | OMCTS | 4.63 | 6.11 | — | 12.1 | (7.0) | (1.0) | 65:35 |
|  | OMCTS | — | 6.04 | 4.05 | (0) | (7.8) | 7.8 | 65:35 |
|  | OMCTS | 4.71 | 6.13 | — | 11.8 | (7.3) | (1.0) | 70:30 |
|  | OMCTS | — | 6.09 | 4.20 | (≤ 0.5) | (7.0) | 6.6 | 70:30 |
|  | OMCTS | 4.59 | 6.10 | — | 12.0 | (6.7) | (1.7) | 50:50 |
|  | OMCTS | — | 6.12 | 4.16 | (≤ 1.3) | (6.7) | 6.7 | 50:50 |
|  | C ₆ H ₆ | 4.13 | 6.27 | 3.91 | 14.0 | -1.8 | 6.5 | 60:40 |
|  | ACN | 4.03 | (1.86) | 3.85 | (-0.8) | 0.9 | (-1.2) | 25:75 |
|  | ACN | 4.44 | — | — | (0) | (7.0) | (0) | — |
|  | ACN | — | — | 4.15 | (0) | (6.8) | (-1.2) | 55:45 |

† Chemical shifts referred to TMS, coupling constants in Hz, values in brackets refer to alkyl groups.

‡ Ratio of superposition used for simulation, see text.

The chemical shifts and coupling constants are internally consistent and very similar to those of vinyl alkyl ethers and related compounds^{19, 30-33}. The chemical shifts also agree with values calculated from group increments²⁰ within ± 0.3 p.p.m., i.e. the limits of confidence for such calculations²⁰. Therefore, the assignments of the olefinic resonances to the enols is beyond all doubt.

The superposition ratios demonstrate that in all cases several pathways of enol formation exist. In accord with expectation the different precursor pairs contribute in equal ratios to the formation of both *cis*- and *trans*-enols. Where possible the two isomers are formed in nearly equal amounts. We do not attempt a further discussion of the fitting parameters *S*, because the relative contributions of T-, F- and S-pair formations of the primary radical pairs remains unknown. Besides, in many of our cases there may be more reactions than those given in sections 3.1 to 3.5 which also contribute to product formation, and our reaction schemes are far from being complete. However, the contribution of disproportionation reactions to enol and product formation is fairly established.

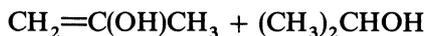
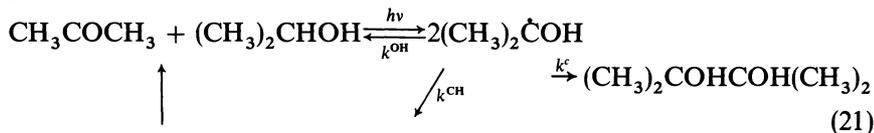
Finally, the lifetimes of the enols indicate that the tautomerizations to the keto forms are rather slow processes though the keto-enol equilibria favour the keto forms to a large extent³⁴.

4. QUANTITATIVE ASPECTS OF ENOL FORMATION, ACETONE-d₆ PHOTOREDUCTION WITH 2-PROPANOL

As stated earlier the CIDNP observation of the enols allows only a rough estimate of the importance of enol formation during the photochemical reactions of aldehydes, ketones and hydroxyketones in solution. In this section we attempt a more quantitative determination by product analysis of the photoreduction of acetone-d₆ with 2-propanol where we expect to be able to discriminate between the various reaction pathways by observing various differently deuterated species.

The photoreduction of acetone-h₆ with 2-propanol has been studied by many authors^{10, 35, 36}. The major stable product is pinacol. Both e.s.r. and u.v. observation of the intermediate radicals^{12, 25, 36} and CIDNP observation of the 2-propenol⁵ suggest the reactions (2)-(4), as repeated in *Scheme 2*.

Scheme 2



Excited acetone reacts from the $\pi\pi^*$ -triplet state with an overall quantum yield³⁶ for acetone consumption of 0.079 ± 0.004 . The rates of OH-disproportionation (k^{OH}), CH-disproportionation (k^{CH}) and combination are unknown for this or similar systems; however, the total termination rate constant $2k = 2(k^c + k^{\text{CH}} + k^{\text{OH}}) = 1.27 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ has been determined for neat 2-propanol solution³⁷. For the 1-hydroxy ethyl radical

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$(k^{\text{OH}} + k^{\text{CH}})/k^c = 0.25^{38}$, $=0.43^{39}$ and $=0.90^{40}$ has been obtained in radiation chemical studies, and for the 1-hydroxy-1-methylethyl radicals of *Scheme 2* this ratio was determined as $6-7^{41}$ and 16^{42} . In published photochemical work Schenck *et al.*⁴³ also assume the predominance of disproportionation over combination and of CH- over OH-disproportionation for the latter radicals⁴³.

Scheme 3

| | | | |
|-------------------|-------|--------------|-------------------|
| | | R_h | R_d |
| k^c | R_h | $R_h - R_h$ | $R_h - R_d$ |
| | R_d | $R_d - R_h$ | $R_d - R_d$ |
| k^{OH} | R_h | $I + A$ | $I + A_{d6}$ |
| | R_d | $I_{d6} + A$ | $I_{d6} + A_{d6}$ |
| $k^{\text{CH,D}}$ | R_h | $I + A$ | $I_{d1} + A_{d5}$ |
| | R_d | $I_{d6} + A$ | $I_{d7} + A_{d5}$ |

For our determination of the relevant parameters of *Scheme 2* we used the system acetone- d_6 -2-propanol- d_0 both 1.0M in the inert solvent acetonitrile- d_3 ³⁶. Here we expect the reaction products given in *Scheme 3*, where R_h denotes $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, R_d is $(\text{CD}_3)_2\dot{\text{C}}\text{OH}$, I is 2-propanol, A is acetone and R—R is pinacol. k^c , k^{OH} and $k^{\text{CH,D}}$ indicate the different termination modes, and the products are formed by the appropriate reactions of the radicals in the column with those listed in the horizontal row. For instance CD-abstraction from R_d by R_h leads to I_{d1} and A_{d5} .

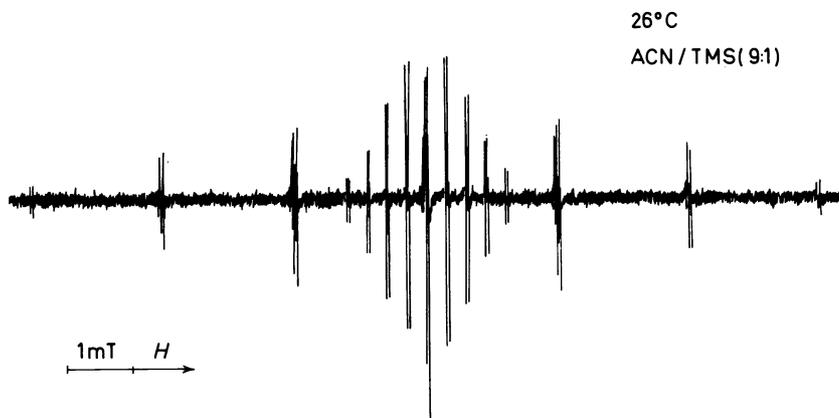


Figure 7. The e.s.r. spectrum of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and $(\text{CD}_3)_2\dot{\text{C}}\text{OH}$ during photolysis of acetone- d_6 -2-propanol.

During photolysis the two radicals R_h and R_d are observed by e.s.r. spectroscopy. *Figure 7* shows an e.s.r. spectrum taken during irradiation of acetone- d_6 and 2-propanol both 1.0M in a 9:1 mixture of acetonitrile and tetramethylsilane (TMS). The spectrum is readily analysed in terms of R_h ($a_p^H = 1.960$ mT, $a_{OH}^H = 0.056$ mT) and R_d ($a_p^D = 0.296$ mT, $a_{OH}^H = 0.058$ mT) and does not show the presence of other radicals. Double integration of the e.s.r. signals shows that R_h and R_d are present in equal concentrations, at least within the experimental accuracy ($R_h/R_d = 1.0 \pm 0.2$). This excludes major isotope effects for the terminations and a fast reaction



H-n.m.r. spectra of irradiated samples show the formation of acetone- d_0 (A), acetone- d_5 (A_{d5}), 2-propanol-2-D (I_{d1}), pinacol- d_6 (R_d-R_h) and pinacol- d_0 (R_h-R_h) as expected from *Scheme 3*. Pinacol- d_{12} (R_d-R_d), 2-propanol- d_6 (I_{d6}) and 2-propanol- d_7 (I_{d7}) were not detected because of severe overlap of the resonances with those of the educt 2-propanol. The upper part of *Figure 8* shows part of a n.m.r. spectrum taken after 49 min irradiation and gives the assignment of the observed transitions. ACN- h_3 was deliberately added to the solutions to serve as internal standard. *Figure 9* shows the yields of the various products as functions of irradiation time and the decrease of the concentration of 2-propanol. The ratios of the product concentration are nearly independent of conversion up to about 50 per cent conversion of

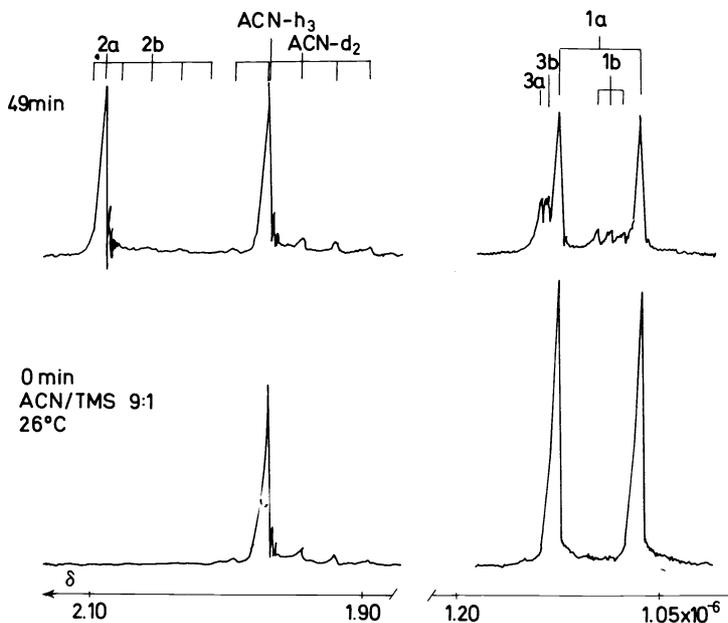


Figure 8. Proton n.m.r. spectrum before and after 49 min irradiation of a solution of 1.0M acetone- d_6 , 1.0M 2-propanol and 0.6M acetonitrile in acetonitrile- d_3 in TMS. 1a represents 2-propanol (CH_3); 1b, 2-propanol-2-D (CH_3); 2a, acetone; 2b, acetone- d_5 ; 3a, pinacol; 3b, pinacol- d_6 .

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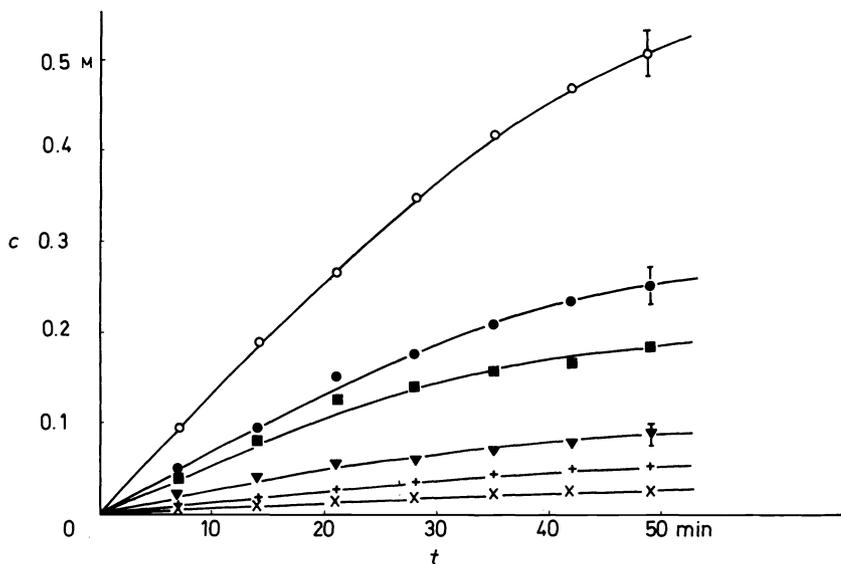


Figure 9. Photoreaction products of acetone-d₆ and 2-propanol versus irradiation time. The upper line gives the decrease in 2-propanol concentration (O), the other lines show the increase of the acetone (●), acetone-d₅ (■), 2-propanol-2D (▼), pinacol-d₆ (+), and pinacol (×) concentrations with irradiation time.

2-propanol. This excludes major secondary reactions of the products. Further the decrease in 2-propanol is balanced within ± 6 per cent by the formation of the observed products. It was checked that no reaction products were formed during 14 days storage of the initial reaction mixture in the dark. After 21 min irradiation a dark reaction leading to acetone-d₅ was found which proceeded about 500 times slower than the photoreaction. Thus, thermal isotope exchange has not to be taken into account in an analysis of the product yields. We believe that the slow dark reactions after irradiation are catalysed by traces of acids or bases formed during irradiation. This is in agreement with a disappearance of the J_{HCOH} -coupling of 2-propanol during irradiation. Photoenolization of acetone-d₆ followed by acid catalysed tautomerization to acetone-d₅ is also excluded because the rate of isotope exchange in a solution of acetone-d₆ (1.0 M) and trifluoroacetic acid (2.0 M) in acetonitrile-d₃ was not enhanced by u.v. irradiation. All these findings support the view that the major reactions are those of Schemes 2 and 3.

From Figure 9 we obtain a value of 2.0 ± 0.2 for the ratio $(R_n - R_d)/(R_n - R_h)$. A value of 2.0 is expected for a statistical control of the combination reactions k^c which thus do not show secondary isotope effects. The ratio of formation of acetone-d₅ (A_{d5}) to 2-propanol-2-D (I_{d1}) is 2.1 ± 0.2 indicating that the two CD-disproportionations of Scheme 3 proceed with the same rates and also do not show secondary isotope effects. If this result is combined with the e.s.r. observation of equal concentrations of R_n and R_d it seems that isotope effects may be neglected, and the reactions are determined by three rate

constants only, k^c , k^{OH} and $k^{\text{CD}} \approx k^{\text{CH}}$. The finding of $k^{\text{CD}} \approx k^{\text{CH}}$ is astonishing since a primary isotope effect is involved which is expected to be appreciable⁴⁴. We plan further experiments to investigate this point in more detail.

Adopting $k^{\text{CD}} = k^{\text{CH}}$ we obtain from *Scheme 3* and *Figure 9* for the ratios of product formation (initial slopes and yields at 20–40 min irradiation)

$$\frac{A - A_{d5}}{A_{d5}} = \frac{k^{\text{OH}}}{k_{\text{CH}}} = 0.3 \pm 0.1 \quad (23)$$

$$\frac{2I_{d1}}{(R_n - R_d)} = \frac{k^{\text{CH}}}{k^c} = 3.4 \pm 0.2 \quad (24)$$

From these values $k^{\text{OH}}/k^c = 1.0 \pm 0.3$ and $(k^{\text{OH}} + k^{\text{CH}})/k^c = 4.4 \pm 0.5$ are obtained. These results indicate that CH-disproportionation is favoured over OH-disproportionation, probably because of the larger number of CH-hydrogen atoms available. The gross ratio of disproportionation versus combination of 4.4 is close to the previous estimate of 6–7⁴¹ and very similar to recent ratios for two *t*-butyl radicals (4.7)¹³ in solution at 23°C. In total, our results imply that about 60 per cent of the 1-hydroxy-1-methylethyl radicals of *Scheme 2* terminate via enol formation by CH-disproportionation, 20 per cent react to educts via OH-disproportionation and 20 per cent give the stable product pinacol. Since the enol tautomerizes to acetone 80 per cent of the initially formed radicals lead to regeneration of the starting materials. This explains the exceptionally low quantum yield of 0.079 for the disappearance of acetone in the photoreaction of acetone and 2-propanol³⁶. In fact, combining this value with our findings we obtain a quantum yield for the primary photoreduction step of $0.079 \times 5 = 0.40$ which is in fair agreement with values found for other solvents³⁶.

The results of this chapter establish that enol formation is an effective pathway for the termination of α -hydroxyalkyl radicals bearing β -hydrogen atoms. They also show that this pathway which may often lead to the regeneration of educts should be considered in aldehyde and ketone photoreactions, in particular, if product yields or educt consumption are to be related to the yields of the primary photoreactions.

After this study was concluded we became aware of the work of Gorzny⁴⁵ who has also investigated the reaction products during photolysis of acetone-d₆ in 2-propanol. Since he used different reaction conditions, in particular fairly high conversions and different temperatures his results are not in complete agreement with the present findings. Also, his analysis of the product yield differs from ours, though the major reactions are the same. Very satisfactory agreement is obtained, however, if we compare the ratios of quantum yields for the various products given by Gorzny⁴⁵ with those predicted from our findings as evident from *Table 3*.

Table 3. Ratios of product quantum yields

| Ratio | $I_{d7}/R-R^\dagger$ | $I_{d6}/R-R$ | $A_{d5}/R-R$ | $A_{d0}/R-R$ | I_{d6}/I_{d7} | A_{d0}/A_{d5} |
|-----------|----------------------|--------------|--------------|--------------|-----------------|-----------------|
| Ref. 44 | 0.95 | 1.2 | 1.3 | 1.6 | 1.3 | 1.3 |
| This work | 0.85 | 1.3 | 1.7 | 2.2 | 1.6 | 1.3 |

† Sum of pinacols.

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