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Electron transfer between a carbon-centered and nitroxide† radicals. A CIDNP study

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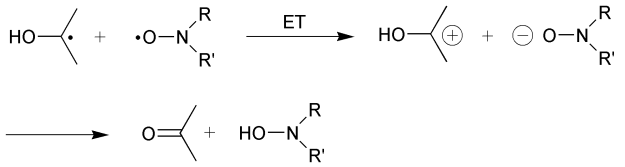
CIDNP effects during the photolysis of 2,2,4,4-tetramethylpentan-3-one (di-*tert*-butyl ketone) and 2,4-dihydroxy-2,-4-dimethylpentan-3-one (di-POH ketone) in solutions containing the nitroxides TEMPO or SG1 [*N*-(2-methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-aminoxyl] show that the *tert*-butyl radical reacts with these compounds by C–O-coupling, whereas the 2-hydroxy-2-propyl radical (POH) reacts by electron transfer followed by proton transfer.

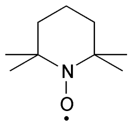
Stable nitroxide radicals are widely used as scavengers for carbon-centered radicals and as mediators of controlled and living radical polymerizations.[1,2] Therefore, the coupling reaction between nitroxides and carbon-centered radicals has gained considerable attention. It is known,[3–7] that the rate constants are substantially smaller than those that are diffusion controlled, and decrease with increasing radical stabilization and steric demand of the substituents, both of the nitroxide and of the carbon-centered species. Moreover, most rate constants show a very unusual temperature dependence with small or even negative activation energies. This has been attributed to unfavorably negative activation entropies for the coupling reaction.[5–7] However, the formation of short-lived intermediates has not been entirely excluded.[7]

It was noted,[7] that in contrast to all other cases, the 2-hydroxy-2-propyl radical (POH) reacts with TEMPO (2,2,6,6-tetramethylpiperidinyl-*N*-oxyl) at a diffusion-controlled rate, and this may reflect a mechanism different from simple coupling. According to the oxidation potential POH is a strongly reducing species[8] ($E_{½}^{ox} = -1.2$ V (SCE)[9]) whereas alkyl radicals are not ($E_{½}^{ox} = +0.09$ V (SCE) for tBu[10]), although the ionization potentials are similar (IP = 6.9 eV for tBu[11] and IP = 6.48 eV for POH[12]). Because of their small reduction potentials,[13] nitroxides can easily be reduced, and hence TEMPO may be rapidly reduced by POH. This electron transfer step may be followed by a proton transfer from POH^+ to $TEMPO^-$ to yield the hydroxylamine TEMPOH and acetone (Scheme 1). Since these products can also result from the usual disproportionation between POH and TEMPO, the mechanism cannot be determined from simple product studies.

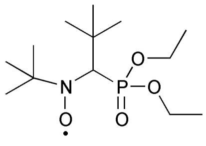


Scheme 1

Therefore, we conducted a comparative study of CIDNP (chemically induced dynamic nuclear polarization) effects during the reaction of 2-methyl-2-propyl (tBu) and 2-hydroxy-2-propyl (POH) radicals with the stable nitroxide radicals TEMPO and SG1 [*N*-(2-methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)aminoxyl].[14] The radicals were generated by laser pulse photolysis of the ketone precursors 2,2,4,4-tetramethylpentan-3-one (di-*tert*-butyl ketone, **1**) for *tert*-butyl and 2,4-dihydroxy-2,4-dimethylpentan-3-one (di-POH-ketone, **2**) for 2-hydroxy-2-propyl in the absence and in the presence of nitroxides TEMPO or SG1.§

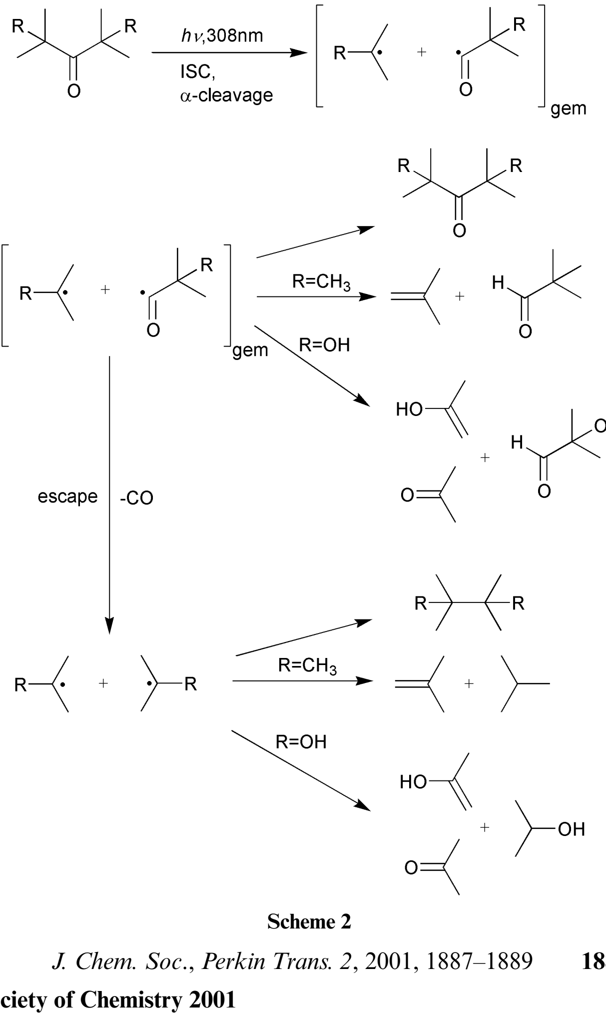


TEMPO



SG1

The photochemistry of the ketones is well known[16,17] (Scheme 2). After excitation in the n–π* absorption region at



Scheme 2

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† The IUPAC name for nitroxide is aminoxyl.

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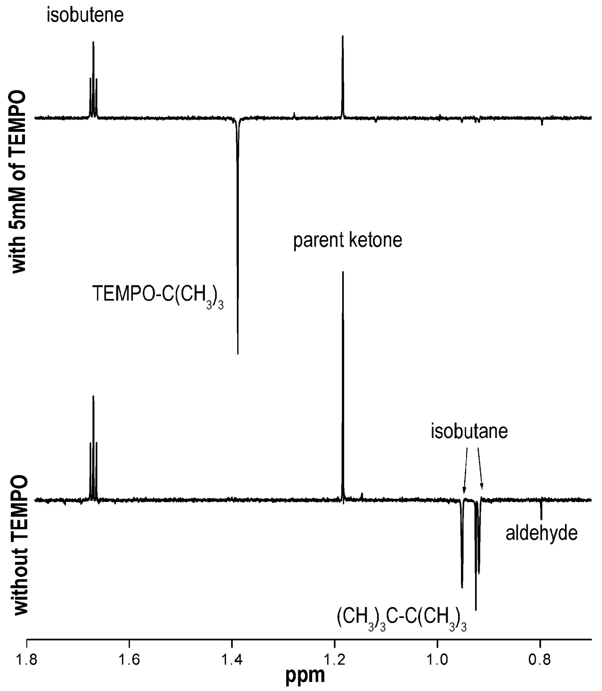

Fig. 1 Up-field part (CH$_3$-region) of a CIDNP-spectrum taken 300 µs after pulse photolysis of di-*tert*-butyl ketone in benzene-d$_6$ in the absence (bottom) and in the presence (top, reduced scale) of TEMPO.

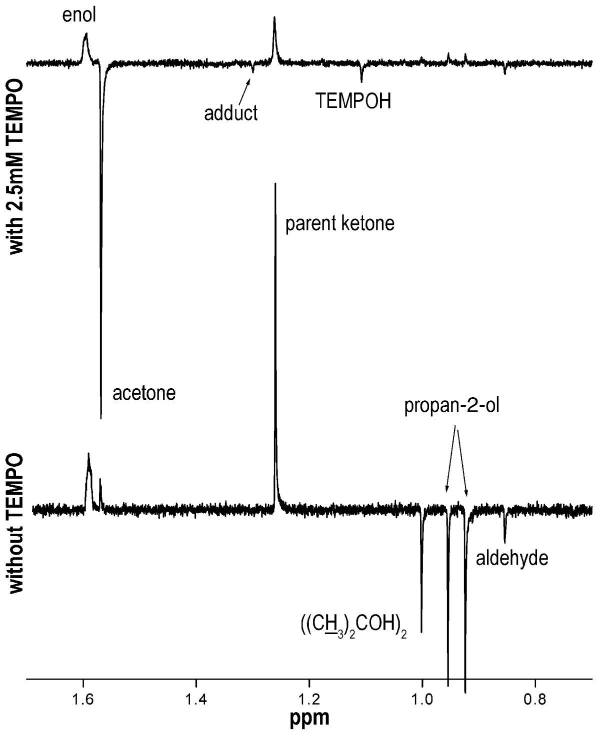

Fig. 2 Up-field part (CH$_3$-region) of a CIDNP spectrum taken 100 µs after pulse photolysis of di-POH ketone in toluene-d$_8$ in the absence (bottom) and in the presence (top, reduced scale) of TEMPO.

308 nm and intersystem crossing, they undergo α-cleavage from the triplet state to yield geminate (cage) acyl–alkyl radical pairs. A small fraction of these pairs recombines to the starting compound and disproportionates to an aldehyde and an alkene. The remainder separate into the bulk. The acyl radicals decarbonylate at room temperature to CO and the corresponding alkyl radicals with rate constants $k_{-\mathrm{CO}} = 4 \times 10^5$ s^{-1} for **1**[16] and $k_{-\mathrm{CO}} = 2.4 \times 10^7$ s^{-1} for **2**.[17] In the bulk, tBu and POH terminate to combination and disproportionation products. Disproportionation usually dominates[16,17] and, for the reaction of two POH radicals, CH-disproportionation is approximately 3 times more efficient than OH-disproportionation.[18]

The CIDNP spectra obtained during the photolysis of both ketones in the absence of nitroxide are in good agreement with previous results.[16,17] The lower part of Fig. 1 is a section of the CIDNP spectrum taken at room temperature 300 µs after laser pulse photolysis of di-*tert*-butyl ketone in benzene-d$_6$. From the *g*-factors and hyperfine coupling constants of the radicals[16] and Kaptein's rules[19] one expects enhanced absorption for the β-CH$_3$-protons of the radical $\dot{C}$(CH$_3$)$_3$ which contribute to the geminate products. This is in fact observed for the parent ketone, the CH$_3$-group of isobutene, as well as for the CH$_2$-group of isobutene and the aldehyde CHO-group which are not shown. The corresponding protons of the escaping tBu radicals carry emissive polarization.[16] Therefore, 2,2,3,3-tetramethylbutane and isobutane exhibit emission. Isobutene is formed both in the geminate and in the bulk disproportionations. Its protons carry enhanced absorption and emission, and the enhanced absorption from the geminate process dominates.

In the presence of 5 mM TEMPO, the formation of 2,2,3,3-tetramethylbutane and isobutane is substantially suppressed. Therefore, their NMR lines have very low intensities in the upper part of Fig. 1. The emissive radical polarization is now transferred by the cross-coupling reaction to the CH$_3$-groups of TEMPO-tBu (1.39 ppm, s). The enhanced absorption of the geminate product ketone is little affected, and that of isobutene is stronger because the emissive contribution from the bulk reaction is now missing. TEMPOH is not observed. These results demonstrate that tBu radicals react with TEMPO nearly exclusively by coupling to the corresponding adduct. If there was considerable disproportionation one would expect a large emission of isobutene as for TEMPO-tBu and an emission of the hydroxy proton of TEMPOH, and this is not found. From the polarization intensities we estimate that the fraction of disproportionation in the reaction between tBu and TEMPO must be smaller than 1%. These results agree with our previous findings of insignificant bulk disproportionation between TEMPO and the carbon-centered radicals Ph$\dot{C}$(CH$_3$)$_2$, RO$_2$C$\dot{C}$(CH$_3$)$_2$, RO$_2$C$\dot{C}$HCH$_3$ and styryl.[20]

The CIDNP effects during the photolysis of **2** in the absence of nitroxide[17] reveal the same mechanism (Fig. 2, lower spectrum). The absorptive polarizations of the parent ketone, the enol and acetone are due to geminate combination, and CH- and OH-disproportionation, respectively, of the POH–acyl radical pair; CH-disproportionation strongly dominates. Propan-2-ol and pinacol carry polarizations of opposite sign because they are formed by disproportionation and combination of the escaping POH radicals. The polarizations of the enol and acetone stem from geminate and bulk processes, and the geminate contributions dominate.

In the presence of TEMPO (Fig. 2, upper spectrum), two new emissive signals appear. The weak singlet at 1.30 ppm could correspond to the POH methyl groups of the coupling product of TEMPO and POH. However, if this questionable assignment holds this product is expected to be unstable and it is not detected in the NMR spectrum after prolonged photolysis. The four methyl groups of TEMPOH appear at 1.11 ppm. This chemical shift agrees with that observed in chlorobenzene during the thermolysis of TEMPO based alkoxyamines,[20] and TEMPOH is also found as a product.

The geminate reactions of the POH–acyl radical pairs are not affected by the presence of TEMPO. Therefore, the absorptive polarization of the parent ketone remains unchanged. In comparison to this, the absorption of the enol CH$_3$-group is increased because the emissive contribution from the bulk disproportionation is scavenged. Pinacol and propan-2-ol now show enhanced absorption. This corresponds to geminate polarizations formed in the POH–acyl radical pair and transferred by fast decarbonylation to the secondary geminate pair POH–POH *via* the memory effect.[17] Acetone now exhibits an emission which balances the enhanced absorptions of the geminate products. Obviously, nearly all CH$_3$-protons of the escaping POH radicals end up in this product. This is most easily explained in terms of the reactions of Scheme 1, namely the electron transfer from POH to TEMPO followed by the rapid transfer of the OH-proton. Of course, the transfer of the OH-hydrogen atom from POH to TEMPO by a normal radical disproportionation cannot be ruled out completely. However, it appears very unlikely because the corresponding CH-disproportionation should be favored energetically and should lead to a strong emission of the enol which is not observed. The CIDNP effects obtained during the photolysis of **2** in the presence of SG1 are completely analogous to those obtained in the presence of TEMPO.

This shows that the different rate constants[7] for reactions of tBu and POH with nitroxides reflect different reaction mechanisms. tBu reacts by coupling but POH reacts *via* electron transfer followed by proton transfer. The latter reaction has the faster rate because it is unaffected by the large negative activation entropy of the coupling process.

Acknowledgements

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Notes and references

§ The experimental arrangement for time-resolved CIDNP has been described before.[15,16] Degassed ketone solutions in benzene-d_6 or toluene-d_8 (OD ≈ 0.2 at 0.4 cm) were irradiated from the side within the CIDNP-probehead (Bruker) of the NMR spectrometer with 20 ns pulses (*ca.* 15 mJ pulse^{-1}) of a Lambda Physik EMG 100 excimer laser at 308 nm. After the individual light pulses, CIDNP spectra were recorded using a 1.85 µs $\pi/2$-NMR-pulse which detects only net polarizations. 24 scans were accumulated for each spectrum, and the samples were shaken after 8 consecutive pulses. The conversions of the parent ketones did not exceed 4%. The concentrations were 14 mM di-*tert*-butyl ketone + 5 mM TEMPO in benzene-d_6; 20 mM di-POH-ketone + 2.5 mM TEMPO (in toluene-d_8) or 2.5 mM SG1 (in benzene-d_6).

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