Photolysis of 2,4-Dihydroxy-2,4-dimethylpentan-3-one Studied by Quantitative Time-resolved CIDNP and Optical Spectroscopy

Michael Salzmann, Yuri P. Tsentalovich[†] and Hanns Fischer
Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057, Switzerland

The mechanisms and kinetics of radical reactions induced by pulse photolysis of 2,4-dihydroxy-2,4-dimethylpentane-3-one have been studied by time-resolved chemically induced dynamic nuclear polarization (CIDNP) and optical spectroscopy. The rate constant for the decarbonylation of the 2-hydroxy-2-methylpropanoyl radical is described by $A = (8.2 \pm 2.0) \times 10^{11}\ s^{-1}$ and $E_a = (23 \pm 3)$ kJ mol^{-1} in methanol, and by $A = (3.7 \pm 1.0) \times 10^{11}\ s^{-1}$ and $E_a = (24 \pm 3)$ kJ mol^{-1} in methylcyclopentane solvents and leads to a CIDNP memory effect. Rate constants for the self-termination of the 2-hydroxyprop-2-yl radicals are derived from the second-order time dependence of the multiplet nuclear polarization of the product propan-2-ol. The time dependence of its net nuclear polarization is influenced by electron–nuclear cross-relaxation. The ratios of disproportionation to the combination of radical pairs are also obtained.

Chemically induced dynamic nuclear polarization (CIDNP) is usually well described by the high field radical pair theory.[1] It is caused by the electron spin selective radical pair formation and decay reactions and intermediate singlet–triplet transitions driven by magnetic interactions. In liquid solutions the kinetics reveal two distinct time scales: processes in geminate pairs in the nanosecond regime which cannot be resolved in time by usual NMR spectroscopic detection, and time evolutions in micro- and milli-seconds which reflect reactions and nuclear relaxation of radicals escaping the geminate pairs. We and others[2] have previously utilized the intensities of CIDNP effects and their time-evolutions to extract rate constants for radical and radical–ion reactions in liquids. Moreover, rate constants for fast rearrangements in geminate radical pairs were obtained *via* the memory effect phenomenon.[2] Interestingly, it was not necessary to invoke electron–nuclear cross-relaxation in these quantitative analyses. This process was originally believed to be the very source of CIDNP[4] but thought unimportant later on, though evidence for its existence has been reported.[5] On the other hand, in the related field of chemically induced dynamic electron polarization (CIDEP) cross-relaxation is an important factor of influence for time-evolutions in systems involving *tert*-butyl, prop-2-yl and 2-hydroxyprop-2-yl radicals.[6]

Here, we present a quantitative study of radical reactions following pulsed photofragmentation of 2,4-dihydroxy-2,4-dimethylpentan-3-one by time-resolved CIDNP. The reaction mechanism is known in principle from earlier work.[7]

$$\mathrm{HO(CH_3)_2C\text{-}CO\text{-}C(CH_3)_2OH} \xrightarrow{h\nu} \mathrm{HO(CH_3)_2C\text{-}\dot{C}O + (CH_3)_2\dot{C}OH} \qquad (1a)$$

$$\mathrm{HO(CH_3)_2C\text{-}\dot{C}O + (CH_3)_2\dot{C}OH} \longrightarrow \mathrm{HO(CH_3)_2C\text{-}CO\text{-}C(CH_3)_2OH} \qquad (1b)$$

$$\mathrm{HO(CH_3)_2C\text{-}\dot{C}O + (CH_3)_2\dot{C}OH} \longrightarrow \mathrm{HO(CH_3)_2C\text{-}CHO + CH_2{=}C(CH_3)OH} \qquad (1c)$$

$$\mathrm{HO(CH_3)_2C\text{-}\dot{C}O} \xrightarrow{k_{co}} \mathrm{(CH_3)_2\dot{C}OH + CO} \qquad (2)$$

$$\mathrm{2\,(CH_3)_2\dot{C}OH} \longrightarrow \text{Products} \qquad (3)$$

We address specifically the rate constant for the decarbonylation [eqn. (2)], the rate constants and the partitioning between combination and disproportionation for the terminations in geminate [eqns. (1b, c)] and non-geminate pairs [eqn. (3)] and the role of cross-relaxation of 2-hydroxyprop-2-yl radicals in CIDNP. Besides time-resolved CIDNP we also apply optical spectroscopy.

Experimental

The arrangement for optical studies has been described earlier.[8] Solutions flowing through a cell (cross section 3 × 10 mm^2) with rates of 3 cm^3 min^{-1} are irradiated with light pulses of a Lambda Physik LPX 100 excimer laser (308 nm, pulse energy $\leqslant$100 mJ). The monitoring system includes a xenon short-arc lamp (Osram XBO 450 W/4) with a high-current pulser, two monochromators, a Hamamatsu R955 photomultiplier, a digitizer LeCroy 9400, and a set of filters and shutters. For low-temperature measurements a nitrogen gas flow through a dewar enclosing the cell was used. The temperature was measured inside the cell just above the irradiated zone. The laser output was monitored by a Gentec ED-500 joulemeter, and initial radical concentrations were determined as in ref. 8. All solutions were freed from oxygen by purging with helium during 1 h prior to use.

Time-resolved CIDNP measurements were carried out with a Bruker CXP-200-FT-NMR spectrometer.[2c,3,9] Samples were irradiated inside the probehead of the spectrometer by an excimer laser beam (Lambda Physik EMG 100, 308 nm). Prior to use, the samples were degassed *via* freeze–pump–thaw cycles, and then sealed off. To avoid secondary photoreactions, the decomposition of the initial compound was kept below 5–7%. To determine the initial radical concentrations, the ketone conversions and product accumulations per laser pulse were measured by conventional NMR spectroscopy. Then the radical concentrations were calculated using the known irradiated volume, $V_B = 0.077$ cm^3. Absolute values of nuclear polarization were obtained by comparing integral intensities of the polarized signals with those of the products in thermal equilibrium after homogenization, taking into account the ratio of the irradiated volume V_B, the detection volume $V_D = 0.16$ cm^3 and the total sample volume $V_T = 1$ cm^3.[3]

$$\Delta M = (1 - I^N_{eq}/I^0_{eq}) \times c_0 \times V_T/(N \times V_B) \qquad (4)$$

[†] *Permanent address:* International Tomography Center, Institutskaya 3, 630090 Novosibirsk, Russia.

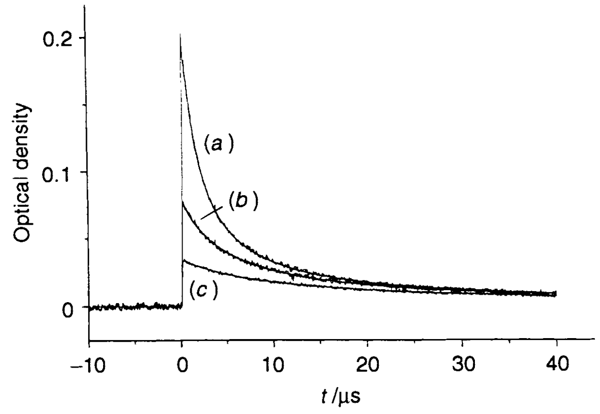

Fig. 1 Transient absorption kinetics of the 2-hydroxyprop-2-yl radical (280 nm) in methanol at room temp. together with the best second-order fit. Initial radical concentrations are (*a*) 2.3×10^{-4}, (*b*) 9.0×10^{-5} and (*c*) 4.2×10^{-5} mol dm^{-3}.

$$P^G/\Delta M = p_{th} \times N \times \frac{V_D}{V_T} \times \frac{I}{I^0_{eq} - I^N_{eq}} \qquad (5)$$

In eqns. (4) and (5) ΔM is the initial radical pair concentration after the laser pulse, $P^G/\Delta M$ is the nuclear polarization per pair, c_0 is the initial ketone concentration, I^0_{eq} and I^N_{eq} are the ketone integrals before irradiation and after N laser pulses, I is the integral of the polarized signal measured immediately after the laser pulse, and p_{th} is the thermal polarization.

To obtain the kinetics of CIDNP with submicrosecond time resolution, 500 ns NMR detection pulses (flip angle 30°) were used, and a deconvolution procedure[2c,10] was applied to take the width and the shape of the detection pulse into account. In CIDNP experiments the optical density of the solutions at 308 nm was about 0.22 (optical pathway about 4 mm inside the sample tube), and during flash photolysis measurements the optical density in the intersection of the laser and monitoring beams (2 mm) was kept below 0.06.

2,4-Dihydroxy-2,4-dimethylpentan-3-one was synthesized following[11] and purified by distillation. The solvents methanol, [$^2H_4$]methanol and methylcyclopentane were used in the purest commercially available forms.

Results and Discussion

Laser Flash Photolysis.—The 2-hydroxyprop-2-yl radical has a broad absorption band between 200 and 400 nm.[12] Radical absorption traces were measured at 280 nm after irradiation of 1.43×10^{-2} mol dm^{-3} solutions of 2,4-dihydroxy-2,4-dimethylpentan-3-one in methanol. At room temperature they decayed by pure second-order kinetics independent of the photolysis dose which indicates that the decarbonylation occurs faster than is observable under these conditions. Assuming then a quantum yield of 2-hydroxyprop-2-yl formation of two, the best fit in Fig. 1 was obtained for a self-termination rate constant $2k_t = (2.2 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1} and a radical absorption coefficient $\varepsilon_{280} = (860 \pm 150)$ dm^3 mol^{-1} cm^{-1}. The termination rate constant is relatively low if compared to radicals of similar size,[8,13] but can be explained by hydrogen bonding which slows down the diffusion of hydroxylated radicals in alcohols.[7]

At temperatures below 250 K a slow growth of the radical absorption after an initial rapid increase is noticeable (Fig. 2). As for the dibenzyl ketone and di-*tert*-butyl ketone,[8,14] this behaviour is attributed to the fast geminate generation of radicals [see eqn. (1)] followed by the slower decarbonylation of the acyl radical [see eqn. (2)]. With the assumption of equal termination rate constants for the acyl and the 2-hydroxyprop-2-yl radicals the change of the concentrations are expressed by eqns. (5) and (6) with $[\mathrm{R\dot{C}O}]_0 = [\mathrm{\dot{R}}]_0$, where $\mathrm{R\dot{C}O}$ is the acyl radical, $\mathrm{\dot{R}}$ is 2-hydroxyprop-2-yl, and k_{co} and $2k_t$ are the de-

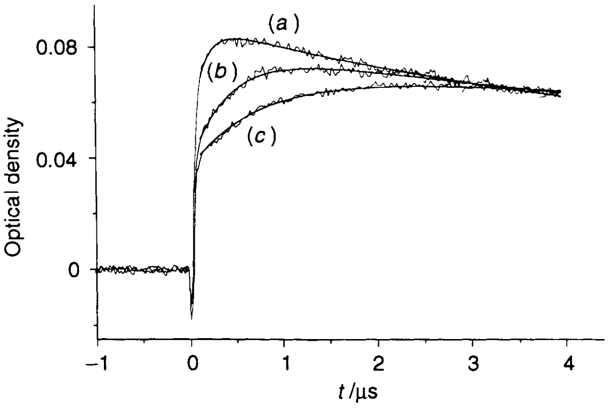

Fig. 2 Initial part of the 2-hydroxyprop-2-yl radical kinetic traces (280 nm) in methanol at (*a*) 242, (*b*) 222 and (*c*) 209 K. For the fitting procedure, see text.

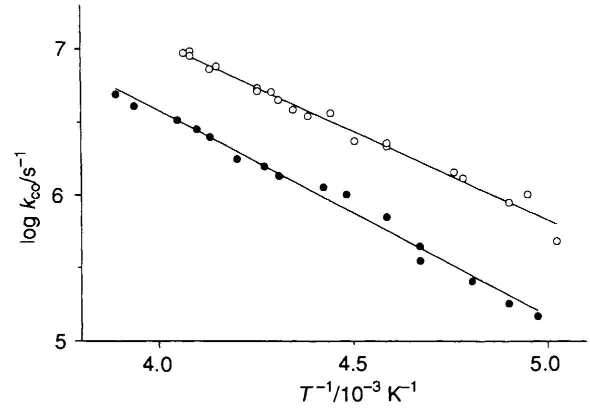

Fig. 3 Arrhenius plots for the decarbonylation rate constant of the 2-hydroxy-2-methylpropanoyl radical: ○ for methanol, ● for methylcyclopentane solvent

$$\frac{d[\mathrm{R\dot{C}O}]}{dt} = -k_{co}[\mathrm{R\dot{C}O}] - 2k_t[\mathrm{R\dot{C}O}]^2 - 2k_t[\mathrm{R\dot{C}O}][\mathrm{\dot{R}}] \qquad (5)$$

$$\frac{d[\mathrm{\dot{R}}]}{dt} = k_{co}[\mathrm{R\dot{C}O}] - 2k_t[\mathrm{\dot{R}}]^2 - 2k_t[\mathrm{R\dot{C}O}][\mathrm{\dot{R}}] \qquad (6)$$

carbonylation and termination rate constants, respectively. A typical fit of the solution of eqns. (5) and (6) to the experimental data at three different temperatures is shown in Fig. 2. Fig. 3 represents Arrhenius plots of the decarbonylation rate constants for methanol and methylcyclopentane solvent obtained for a temperature range from 199–257 K. For methanol the frequency factor is $A = (8.2 \pm 2.0) \times 10^{11}$ s^{-1}, and the activation energy is $E_a = (23 \pm 3)$ kJ mol^{-1}, whereas for methylcyclopentane $A = (3.7 \pm 1.0) \times 10^{11}$ s^{-1} and $E_a = (24 \pm 3)$ kJ mol^{-1}. Extrapolation to room temp. gives $k_{co} = 7.1 \times 10^7$ s^{-1} for methanol and $k_{co} = 2.4 \times 10^7$ s^{-1} for methylcyclopentane solvent. The temperature averaged value of the 2-hydroxyprop-2-yl absorption coefficient at 280 nm is (860 ± 150) dm^3 mol^{-1} cm^{-1} for methanol and (500 ± 100) dm^3 mol^{-1} cm^{-1} for methylcyclopentane solvent. The temperature dependence of the termination rate constant reflects that of the diffusion coefficients for the corresponding

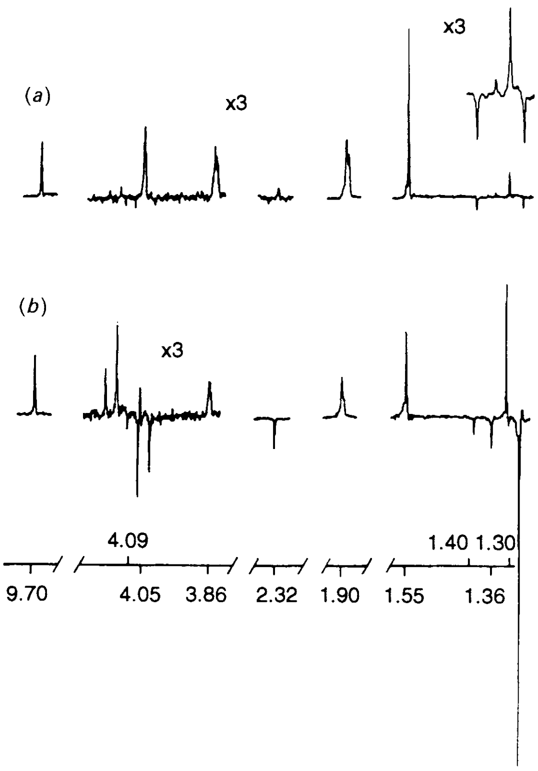

Fig. 4 CIDNP spectra obtained after flash-photolysis of 2,4-dihydroxy-2,4-dimethylpentan-3-one in [$^2H_4$]methanol; (*a*) immediately after the laser pulse and (*b*) 1 ms thereafter

solvents. For the solvent methanol the Arrhenius parameters of $2k_t$ are $A = (3.2 \pm 0.6) \times 10^{11}$ dm^3 mol^{-1} s^{-1} and $E_a = (11.4 \pm 2.0)$ kJ mol^{-1}, and for methylcyclopentane $A = (4.0 \pm 0.6) \times 10^{12}$ dm^3 mol^{-1} and $E_a = (15.7 \pm 3.0)$ kJ mol^{-1}.

Somewhat surprisingly, the decarbonylation rate constant for methanol is higher than that for the non-polar solvent methylcyclopentane. In previous work[8] we have shown that the decarbonylation rate of phenylacetyl and pivaloyl radicals decreases with increasing solvent polarity. This was attributed to a lower dipole moment of the transition state for decarbonylation compared with that of the parent acyl radical, and hence to a weaker stabilization of the transition state by the more polar solvents. In fact, for non-associating liquids the dependence of the reaction rate constants on solvent polarity was well described by Kirkwood's formula.[15] However, for alcoholic solvents deviations from Kirkwood's formula to larger rate constants were found,[8] and attributed to the influence of hydrogen bonding of the acyl groups. For the hydroxylated acyl radical 2-hydroxy-2-methylpropanoyl a stronger hydrogen bonding effect is not unreasonable and seems to surpass the effect of unspecific solvation. From the activation parameters the effect is mainly entropic and points to a modified structure of the transition state.

CIDNP.—Polarizations. CIDNP spectra obtained at room temperature immediately and 1 ms after pulse photolysis of 2.74×10^{-2} mol dm^{-3} 2,4-dihydroxy-2,4-dimethylpentan-3-one in CD_3OD are shown in Fig. 4. The individual transitions belong to the parent ketone (CH_3-groups 1.55 ppm) and the reaction products 2-hydroxy-2-methylpropanal (CH_3-groups 1.40 ppm, CHO proton 9.70 ppm), the enol of acetone (CH_3-group 1.90 ppm, CH_2-group 3.86 and 4.05 ppm), propan-2-ol (CH_3-groups 1.30 ppm, CH-proton, 4.09 ppm), acetone (2.32 ppm) and pinacol (CH_3-groups 1.36 ppm). Integration of the signals at various delay times showed that the polarizations of the parent ketone and of the aldehyde are time-independent whereas all others exhibit strong time-evolutions. This demonstrates that the ketone and the aldehyde are formed in geminate reactions only, and that the rate of decarbonylation of the primary acyl radical occurs faster than is measurable by our NMR technique. The upper time limit is 200 ns and agrees with the rate constant derived from optical spectroscopy.

With the aid of Kaptein's rules[16] and the magnetic properties $g = 2.003\,17$, $a(CH_3) = +1.966$ mT for $(CH_3)_2\dot{C}OH$[17] and $g = 2.0008$, $a(CH_3) = +0.096$ mT for $HO(CH_3)_2C\dot{C}O$[7] the net and multiplet effects of the parent ketone, the aldehyde, the acetone and the enol are attributed easily to geminate reactions of the primary triplet hydroxy-alkyl/acyl radical pair [eqns. (7)–(10)].

$$HO(CH_3)_2CCOC(CH_3)_2OH^T \longrightarrow \overline{HO(CH_3)_2C\dot{C}O \quad \dot{C}(CH_3)_2OH}^{G_1} \qquad (7)$$

$$\overline{HO(CH_3)_2C\dot{C}O \quad \dot{C}(CH_3)_2OH}^{G_1} \xrightarrow{k_c^{G_1}} HO(CH_3)_2CCOC(CH_3)_2OH \qquad (8)$$

$$\overline{HO(CH_3)_2C\dot{C}O \quad \dot{C}(CH_3)_2OH}^{G_1} \xrightarrow{k_{d9}^{G_1}} HO(CH_3)_2CCHO + CH_2{=}C(CH_3)OH \qquad (9)$$

$$\overline{HO(CH_3)_2C\dot{C}O \quad \dot{C}(CH_3)_2OH}^{G_1} \xrightarrow{k_{d10}^{G_1}} HO(CH_3)_2CCHO + CH_3COCH_3 \qquad (10)$$

For these products the protons originating from the CH_3-groups of $(CH_3)_2\dot{C}OH$ all show rather strong enhanced absorptions, while owing to the small hyperfine coupling constant a weak emission is observed for CH_3-protons of the acyl moiety. With neglect of this small emissive contribution to the ketone signal and omission of a possible small aldehyde polarization from OH-protons the ratio of absorptions $6I(CHO)/I(\text{ketone})$ reflects the ratio of disproportionation to combination of the primary pair [eqns. (8) and (9)]. From several determinations with short delay times $k_{d_9}^{G_1}/k_c^{G_1} = 2.4 \pm 0.4$ was obtained. Because of the weakness of the signal of acetone the ratio of OH- to CH-disproportionation [eqns. (9) and (10)] could not be determined accurately, but is certainly smaller than 0.1.

2-Hydroxyprop-2-yl radicals escaping the geminate process carry a substantial emissive polarization. In non-geminate reactions this is transferred to the products of their combination and disproportionation reactions [eqns. (11)–(13)]. Therefore,

$$2\,(CH_3)_2\dot{C}OH \longrightarrow HO(CH_3)_2CC(CH_3)_2OH \qquad (11)$$

$$2\,(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CHOH + CH_2{=}C(CH_3)OH \qquad (12)$$

$$2\,(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CHOH + CH_3COCH_3 \qquad (13)$$

the enhanced absorption of the enol protons decreases in time, and pinacol, propan-2-ol and acetone exhibit increasing emission [Fig. 4(*b*)]. The non-geminate reactions of equal radicals do not lead to additional net effects[1] but they also create an additional *E*/*A* multiplet polarization of propan-2-ol and enol which also increases in time. A close inspection of Fig. 4(*a*) and especially of the inset reveals that the pinacol and propan-2-ol appear in absorption at an early time which later converts to emission due to the above mentioned polarization transfer. Also, the *E*/*A* multiplet polarization of propan-2-ol

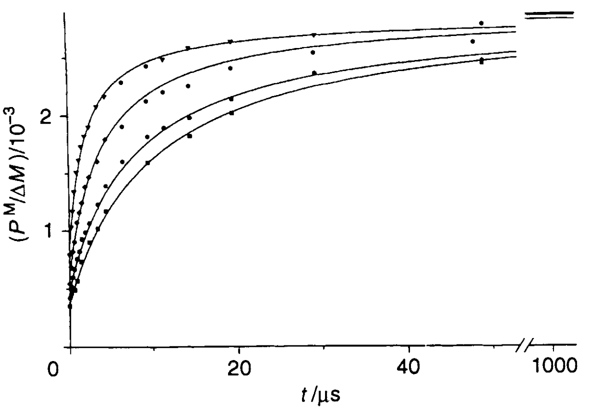

Fig. 5 Time dependence of the multiplet CIDNP effect for the CH_3-protons of propan-2-ol (calculated curves, see text). Initial radical concentrations are 3.4×10^{-4} (▼); 1.2×10^{-4} (◆); 5.6×10^{-5} (●) and 3.0×10^{-5} mol dm^{-3} (■).

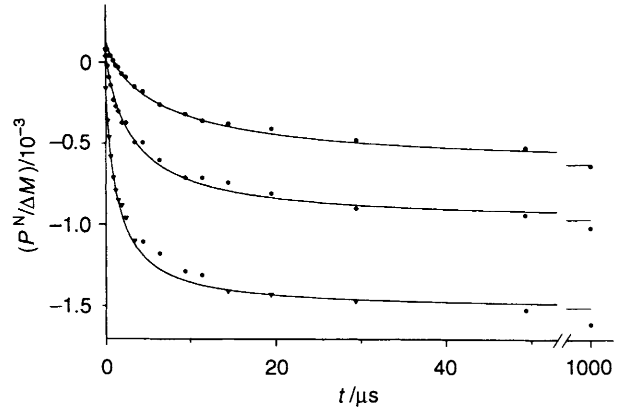

Fig. 6 Time dependence of the net CIDNP effect for the CH_3-protons of propan-2-ol (calculated curves, see text). Initial radical concentrations are 3.4×10^{-4} (▼); 1.2×10^{-4} (◆) and 5.6×10^{-5} mol dm^{-3} (●).

starts from a non-zero value (Fig. 5). Both products and their polarizations cannot be ascribed to the reactions (8)–(10) of the primary hydroxyalkyl–acyl radical pair. They are explained quite naturally, however, by the fast decarbonylation [eqn. (2)] of the acyl moiety which converts rapidly the primary pair to a secondary pair of two 2-hydroxypropyl radicals. The combined spin evolutions in both pairs and the reactions (11)–(13) of pair G_2 then causes the observed memory effect type polarization.[3]

$$\overline{HO(CH_3)_2C\dot{C}O\quad \dot{C}(CH_3)_2OH}^{G_1} \longrightarrow \overline{HO(CH_3)_2\dot{C}\quad \dot{C}(CH_3)_2OH}^{G_2} + CO \qquad (14)$$

To extract the decarbonylation rate constant from the CIDNP intensities the total net polarizations created by the primary (P_1^G) and the secondary (P_2^G) pair processes per initial pair ΔM were measured at short times for five different initial radical concentrations in the range $5.6 \times 10^{-5} \leqslant [\dot{R}]_0 \leqslant 3.45 \times 10^{-4}$ mol dm^{-3}. The averages are $P_1^G/\Delta M = (4.4 \pm 0.7) \times 10^{-3}$ and $P_2^G/\Delta M = (3.5 \pm 1.5) \times 10^{-4}$. Since these quantities are rather sensitive to the decarbonylation rate constant they were also calculated using procedures described earlier.[3] Apart from the magnetic parameters of the radicals given above we used the radii of 270 pm for the acyl and of 250 pm for the 2-hydroxyalkyl radical, equal diffusion coefficients $D = 5 \times 10^{-6}$ cm^2 s^{-1} and an initial inter-radical distance of 570 pm. A good agreement between the experimental results and the calculated values of $P_1^G/\Delta M = 4.3 \times 10^{-3}$ and $P_2^G/\Delta M = 3.4 \times 10^{-4}$ was found for $k_{co} = 1.1 \times 10^8$ s^{-1} and a fast relaxation rate of $T_2^{-1} = 1.9 \times 10^9$ s^{-1} for the acyl radical. The T_2^{-1} value is rather similar to values found for other acyl radicals,[3,9d,e] and the rate constant for decarbonylation agrees fairly well with that extrapolated from the low temperature data obtained by optical spectroscopy and methanol solutions.

In earlier work[7] we reported a rather indirect determination of k_{co} in a high viscous solvent which lead to log $A = 11.4$ s^{-1}, $E_a = (31 \pm 6)$ kJ mol^{-1} and an extrapolated k_{co} (298 K) = 9.6×10^5 s^{-1}. In view of the present results the older rate constant is too low by nearly two orders of magnitude and is not tenable. If it were correct a memory effect type CIDNP would not have been observable.

Kinetics. The analysis of time-dependencies of CIDNP effects yields additional information on radical reaction and relaxation rates.[2b,c,5d,e,9] Because of the high rate of decarbonylation of the acyl radical they are governed by the dynamics of the 2-hydroxyprop-2-yl radicals only. These radicals escape the geminate processes with a substantial emissive polarization of their CH_3-protons and transfer this polarization to the products *via* reactions (11)–(13). Part of it can be lost by relaxation. Multiplet-type polarizations in the products propan-2-ol and enol are formed mainly in non-geminate encounters. Here, we analyse the net and multiplet effects of the CH_3-protons of propan-2-ol at $\delta = 1.30$ which exhibit the strongest time-dependence (Fig. 4).

Fig. 5 shows the kinetics of the multiplet-type polarization defined as the difference of the intensities of the absorptive and emissive lines for four different initial radical concentrations. Scaled by the initial pair concentration $\Delta M = \frac{1}{2} \times [\dot{R}]_0$ the four traces start from common values and end at common values. The multiplet polarization of 2-hydroxyprop-2-yl radicals from geminate and non-geminate reactions corresponds to an even spin-order of the six protons. In propan-2-ol these protons are magnetically equivalent, and, hence, this polarization is unobservable. Thus, the only source of the multiplet-type polarization in propan-2-ol is the spin selection of nuclei belonging to the two radicals in the non-geminate pairs, and this is not influenced by nuclear relaxation.[5e,b] Therefore, the time-evolutions of Fig. 5 are solely due to the second-order self-termination kinetics of 2-hydroxyprop-2-yl. This leads to the expression shown in eqn. (15),[9] where the last

$$\frac{P^M}{\Delta M} = \text{sign}(J) \times f_M \times \frac{2k_t[\dot{R}]_0 t}{1 + 2k_t[\dot{R}]_0 t} + \frac{P^{M,G}}{\Delta M} \qquad (15)$$

term denotes the multiplet polarization created in the secondary pair [eqn. (14)]. Sign (J) is the positive sign of the J-coupling in propan-2-ol, $2k_t$ the self-termination rate constant and f_M the multiplet polarization created in the overall termination process. The curves shown in Fig. 5 were obtained by fitting all data to eqn. (15) and reflect the parameters $P^{M,G}/\Delta M = (5.0 \pm 1.0) \times 10^{-4}$, $f_M = (6.8 \pm 1.7) \times 10^{-3}$ and $2k_t = (2.24 \pm 0.36) \times$ dm^3 mol^{-1} s^{-1}. They seem very reasonable. The large ratio of $f_M = P^{M,F}/\Delta M$ to $P^{M,G}/\Delta M$ confirms the order of magnitude of the decarbonylation rate constant, and $2k_t$ agrees with the data obtained by optical spectroscopy.

The time-evolution of the net polarization of propan-2-ol measured as the sum of the intensities of the CH_3-doublet at $\delta = 1.30$ is shown in Fig. 6 for three initial radical concentrations. As for the multiplet effect the curves start at a common initial value but they do not reach a common final point. Owing to the spin-sorting character of CIDNP the 2-hydroxyprop-2-yl radicals initially carry a net nuclear polarization which is opposite in sign but equal in magnitude to the net geminate polarization per radical pair $P^G/\Delta M = (4.7 \pm 0.8) \times 10^{-3}$ (see above). If this were fully transferred to products by the non-geminate reactions (11)–(13) the branching between disporportionation and combination and the distribution of protons between propan-2-ol and enol would lead to a common final net polarization of propan-2-ol of $-k_d/2(k_c + k_d) \times P^G/\Delta M \approx 2 \times 10^{-3}$. From Fig. 6 it is clear that this value is not reached, and that lower initial radical concentrations lead to larger losses of polarizations. Since we could not detect products of side reactions which could cause such a behaviour in principle, the loss of polarization has to be attributed to spin relaxation in the intermediate 2-hydroxyprop-2-yl radicals.

In previous work, we and others[2a,c,9a,b,18] have considered nuclear relaxation by T_1-processes in radicals as the only source of such polarization losses and have obtained relaxation times $T_1 = 90$ µs for $\dot{C}H_3$[18a] and $T_1 = 100$ µs for $\dot{C}(CH_3)_3$ radicals.[9a] Application of the appropriate equations[9a] to the data of Fig. 6 leads to very unsatisfactory results. Much shorter relaxation times below 20 µs would have to be invoked to explain the behaviour at short times, and they would lead to a levelling-off of the time-evolution below 20 µs whereas the emissions continue to increase even after 100 µs. Therefore, we suggest that an additional relaxation mechanism must operate which in effect diminishes the emission polarization of the radicals on the 10–100 µs time-scale. Based on recent studies of CIDNP[5d,e] and CIDEP[19] in other reaction systems involving 2-hydroxyprop-2-yl radicals cross-electron-nuclear relaxation by modulation of the scalar hyperfine interactions is the natural choice. It leads to simultaneous electron-nuclear spin transitions with $\Delta m^S + \Delta m^I = 0$ and causes enhanced absorption for the nuclear spins if the electron spin system initially carries a negative spin polarization.[19c] Both from the triplet and the radical pair mechanism of CIDNP electron spin emission can in fact be expected for our case of geminate reactions.[20]

The inclusion of cross-relaxation requires the explanation of the time-dependence of the net nuclear polarization of propan-2-ol in terms of the following set of coupled equations for the radical concentrations $[\dot{R}]$, the product nuclear polarization P^N and in radicals P^N_R, and of the electron polarization P^S_R [see eqns. (16)–(19)].

$$\frac{d[\dot{R}]}{dt} = -2k_t[\dot{R}]^2 \tag{16}$$

$$\frac{dP^N}{dt} = 2k_t[\dot{R}] \times P^N_R \tag{17}$$

$$\frac{dP^N_R}{dt} = -2k_t[\dot{R}] \times P^N_R - \frac{P^N_R}{T^N_1} - \frac{P^N_R + 6P^S_R}{T_x} \tag{18}$$

$$\frac{dP^S_R}{dt} = -\left(\frac{1}{T^S_1} + 2k_r[\dot{R}]\right) \times P^S_R - \frac{P^N_R + 6P^S_R}{T_x} \tag{19}$$

Here, the first terms of eqns. (17) and (18) describe the transfer of nuclear polarization from radicals to products, and the last terms of eqns. (18) and (19) are due to the cross-relaxation. The remaining terms in eqns. (17) and (18) denote pure nuclear and electron spin relaxations. For the latter we assume a rate which increases with the radical concentration due to intermolecular dipole–dipole interactions.[21] Boltzmann equilibrium polarizations are neglected. The cross-relaxation term was derived rigorously and includes a factor of six with P^S_R which is due to the hyperfine interaction with six equivalent protons. For a simulation of the time-evolutions of Fig. 6 $2k_t = 2.2 \times 10^9$ dm^3 mol^{-1} s^{-1} and $P^N_R(0) = -2 \times 10^{-4} \times \Delta M$ were adopted from the findings given above. $T^S_1 = 2.7$ µs was taken from ref. 22, and $T^N_1 = 500$ µs and $P^S_r(0) = 5 \times 10^{-2} \times \Delta M$ were assumed as reasonable. Of these values T^N_1 did not play a significant role, because the influence of the cross-relaxation is much stronger than of the nuclear relaxation. The values for T_x and $2k_r$ were then obtained by fits of eqns. (16)–(19) to the data which resulted in $T_x = (290 \pm 40)$ µs and $2k_r = (1.1 \pm 0.1) \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The cross-relaxation constant agrees with a previous estimate[5e] and is also in accord with similar values for other radicals.[5,19] Interestingly, $2k_r$, which reflects the influence of radical concentration on electron spin relaxation is larger than $2k_t$, the rate constant for self-termination. For acetate radical anions $^{\bullet}CH_2CO_2^-$ Syage *et al.*[21b] found a similar ratio, and this may support our analysis.

In total, we conclude that the chemical reactions and the geminate nuclear polarizations following α-cleavage of 2,4-dihydroxy-2,4-dimethylpentan-3-one are quantitatively described by this work. It also presents an additional example for the cross-relaxation mechanism of CIDNP which remains to be fully explored, however.

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