Termination Rates by Time-Resolved ESR. The N-Hydropyridinyl Radical in Solution and the Influence of Non-Uniform Radical Concentration on the Apparent Rate Constant

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The rate constants (2 k) for the second-order self-termination reaction of the N-hydropyridinyl radical have been measured by time-resolved ESR during intermittent UV photolysis of pyridine in various solvents containing propanol(-2). The frequency factor and the activation energy are $(1.8 \pm 0.4) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $(10.7 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$, respectively, in propanol(-2)/acetone (1:1 by volume) as obtained from the Arrhenius plot of 2 k in the temperature range between 293 and 230 K. The rate constants at 285 K are $(7 \pm 1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in H₂O/propanol(-2)/acetone (2:1:1 by volume), independent of the pH value (7.5 - 13.7), and $(6 \pm 1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in neat propanol(-2), the latter value being essentially diffusion controlled. The rate constants measured in propanol(-2)/acetone (1:1) containing various amounts of water correlate with Kosower's solvent polarity parameter. The self-termination reaction ultimately leads to the destruction of the pyridine ring. Finally, a model is presented for the correction of the influence of non-uniform radical concentration on apparent values of second-order rate constants as determined by time-resolved ESR during intermittent photolysis.

1. Introduction

Our continuing interest in kinetic [1, 2], thermodynamic [2] and other molecular properties [3-5] of radicals derived from pyridine compounds has stimulated an investigation of the termination reaction of the unsubstituted N-hydropyridinyl radical. This species is the one-electron reduced form of the pyridinium cation. An optical transient ascribed to this radical has previously been observed during electron-pulse radiolysis of pyridine in aqueous solution [6]. Unequivocal evidence as to the nature of this short-lived species stems from in-situ ESR studies either during continuous electron irradiation [7] or during continuous UV photolysis [8] of pyridine in solution. For the present investigation we produced the radical by intermittent UV photolysis in various solvent mixtures containing propanol(-2) as a reducing agent. When compared with other pyridine compounds [1-4], the photochemical yield of the radical was quite low, particularly so in neat propanol(-2). Upon the attempt to increase the radical concentration by using larger concentrations of pyridine in propanol(-2), we observed an apparent increase in the second-order termination rate constant of the radical. A tentative explanation was that the increased absorption of the photolysis light produced a non-uniform radical concentration in the ESR cell which, in turn, caused a spatially varying rate of the termination reaction. Such an effect has been known since the advent of the flash photolysis technique [9]. For detection of intermediates by kinetic spectrophotometry, the effect has been studied earlier by Boag [10]. Meanwhile we presented a solution to this problem for the case of radical detection by time-resolved ESR during intermittent photolysis [11]. Recently, Basu and McLauchlan also considered this problem with reference to radicals made by flash photolysis [12]. Although they used essentially the same model as we did, they arrived at a conclusion different from ours.

In the present paper, we report the rate constants of the second-order termination reaction of the N-hydropyridinyl

radical and their temperature dependence in some solvents containing propanol(-2). We also communicate a model suitable to correct measured second-order rate constants for the influence of non-uniform radical concentration and demonstrate its application on the kinetic in-situ ESR measurement during the photolysis of pyridine in propanol(-2).

2. Experimental Section

The arrangement for the kinetic in-situ ESR experiment was as described earlier [1]. All the measurements, except those required for the Arrhenius plot of the rate constants, were made at 12°C in fused silica flat cells *not* surrounded by a cooling jacket. (For the temperature control system, see Ref. [3a].) In each case, a parallel beam of chopped light from a 1-kW mercury/xenon lamp (Hanovia 977 B-1, dc-operated) was used for the photolysis. When desired, light near 270 nm (in the absorption band of pyridine) was applied. For the determination of the radical concentration by twofold integration of the ESR signal and comparison with the internal ruby standard, resolved lines were selected from the outermost low and high-field portions of the ESR spectrum.

The following chemicals were used as purchased from Merck: pyridine (99.5%), propanol(-2) (99.7%, less than 0.01% acetone), acetone (99.5%), buffer solutions at pH 6 (citrate/NaOH), pH 7 (phosphate), pH 9 (borate/KOH/KCl), and HClO₄ (p.a.). The solutions to be photolyzed were carefully deaerated by purging with purified nitrogen. Contamination of the solutions by oxygen was minimized by using sealed joints in the flow system. The solutions were photolyzed as they flowed slowly through the ESR cell. The dwell time of the solution in the flat portion of the ESR cell was much longer than the decay time of the radical during the dark period.

The solvent polarity parameter, Z, introduced by Kosower [13] was determined by measuring the wavelength of the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide in the solvent under study (Zeiss DMR 22 UV-VIS spectrophotometer, measurement in the presence of $3 \cdot 10^{-4}$ M Na₂S₂O₃). The pyridinium salt was prepared from ethyl iodide and methylisonicotinate (98%, EGA-Chemie) in acetone and was purified by recrystallization from methanol (m.p. 111°C).

The viscosity of the solvents was measured over the temperature range of ca. 5 to 40°C (KPG-Ubbelohde-Viskosimeter, Schott, Mainz).

3. Results

3.1. Rate Constants in Solutions Containing Propanol(-2) and Acetone

Fig. 1 (top) shows the ESR spectrum of the N-hydropyridinyl radical taken during continuous photolysis in propanol(-2)/acetone (1:1 by

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Fig. 1

Experimental (top) and calculated (bottom) ESR spectrum of the N-hydropyridinyl radical in propanol(-2)/acetone (1:1 by volume) at 35°C. (Low-field half. For the analysis of the hyperfine pattern, see Refs. [5, 7, 8]. The asterisk denotes the line used for the time-resolved measurement of Fig. 2)



Fig. 2

Time dependence of the concentration of the N-hydropyridinyl radical during intermittent UV photolysis at 12°C of pyridine (0.6 M) in propanol(-2)/acetone (1:1 by volume). Average of 22000 transients. (Open circles: second-order plot of the decay curve during the dark period)

volume) at 35°C. No signal was present of the (CH₃)₂COH counter radical under the conditions used for the present study. Fig. 2 presents an example for the time-resolved ESR measurement performed at 12°C and at constant magnetic field, at the position of the maximum of the 8th low-field hyperfine line (asterisk in Fig. 1). During the light period of the intermittent photolysis, a steady-state concentration of 8.7 μ M was established. In the dark period a decay of the signal corresponding to a second-order self-termination reaction of the radical was seen. (The initial part of the decay curve has been omitted from the kinetic analysis because of the sector error.) The termination rate constant obtained from the slope of the linearized plot of the decay data $(2kc_0 =$ $1.9 \cdot 10^3 \text{ s}^{-1} \pm 5\%$ from the straight line in Fig. 2) and the initial concentration, $c_0 = 7.3 \ \mu\text{M}$, of the radical is $2k = 2.6 \cdot 10^8 \ \text{M}^{-1} \ \text{s}^{-1}$. Similar measurements have been made in the temperature range -43 to 20°C in propanol(-2)/acetone (1:1 by volume). Fig. 3 shows the Arrhenius plot. We obtain

$$2k/M^{-1} s^{-1} = (1.8 \pm 0.4) \cdot 10^{10} \cdot \exp\left(-\frac{10.7 \pm 0.4/kJ \cdot mol^{-1}}{RT}\right)$$

for the temperature dependence of the rate constant. The broken line in Fig. 3 represents the diffusion controlled second-order rate constant estimated by use of the Smoluchowsky-Stokes-Einstein relation [14],

$$2k_{\rm d}/{\rm M}^{-1}\,{\rm s}^{-1} = \sigma \cdot 8 \cdot 10^3 \cdot RT/3 \cdot \eta(T)$$
.

 $\eta(T)$ denotes the measured temperature-dependent viscosity (in Pa · s) of the solvent, $\sigma = 1/4$ is the spin statistical factor (reaction of singlet encounter pairs), and the factor 10^3 converts the SI-unit of volume, m³, to dm³. From the slope of the broken line in Fig. 3 we obtain 12.0 ± 0.1 kJ · mol⁻¹ for the activation energy of diffusion in propanol(-2)/acetone (1:1 by volume) and a frequency factor of $4 \cdot 10^{11}$ M⁻¹ s⁻¹.



Arrhenius plot of the rate constants for the self-termination reaction of the N-hydropyridinyl radical in propanol(-2)/acetone (1:1 by volume). Broken line: diffusion controlled rate constant as calculated from the solvent viscosity by use of the Smoluchowsky-Stokes-Einstein relation

The following additional results all were obtained at a temperature of 12°C:

- (a) The termination rate constant in propanol(-2)/acetone (1:1 by vol.) was independent of the pyridine concentration in the range examined (0.2-1.2 M pyridine). At pyridine concentrations of below 0.1 M the ESR spectrum of the (CH₃)₂COH counter radical showed up.
- (b) At a fixed concentration of pyridine (0.5 M) the rate constant was independent of the fraction of acetone (5 - 48%) by vol.) present in propanol(-2), although the viscosity of the solvent mixture strongly depends on the concentration of acetone. Neither in case (a) nor in case (b) was the measured termination rate constant influenced by the thickness of the ESR flat cell (see, however, Section 3.2).



Correlation between the self-termination rate constant and the solvent polarity parameter Z. (See Ref. [13] for definition of Z). Propanol(-2)/ acetone (1:1 by volume) containing 0, 25, and 50% by volume of water at $12^{\circ}C$

- (c) Upon addition of water (0-50% by vol.) to the solvent mixture made up of equal parts (by volume) of propanol(-2) and acetone, an increase of the second-order termination rate constant was found, $(2.2 \pm 0.2) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in the absence of water and $(7 \pm 1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of 50% of water. Over this range, 2k correlates with Kosower's solvent polarity parameter, Z, see Fig. 4.
- (d) In buffered solution (solvent made up of water, propanol(-2), and acetone, volume fractions of 2:1:1, respectively), the self-termination rate constant was independent of the pH value over the range studied (pH 7.5 13.7). At the pH of 7.5 a line broadening effect was noted which is tentatively explained by electron exchange between the pyridinium ion (p $K_a = 5.3$) and the N-hydropyridinyl radical. Because of the poor signal-to-noise ratio no kinetic ESR measurements were made at pH values of below 7.5.

3.2. Rate Constants in Propanol(-2)

The radical could also be produced in neat propanol(-2). Here, pyridine was excited directly at ca. 270 nm. Most likely, the excited state abstracts a hydrogen atom from the solvent. (A signal of the $(CH_3)_2COH$ counter radical was seen, when the concentration of pyridine was less than 2%.)

As in propanol(-2)/acetone mixtures, a second-order rate law was found for the self-termination of the N-hydropyridinyl radical. This is at variance with an earlier finding [15]. The prerequisite for the secondorder law was the most careful exclusion of oxygen from the solution. Other than in propanol(-2)/acetone, the rate constants obtained from the second-order plot of the decay curves apparently increased when the concentration of the parent pyridine was increased or when ESR cells of larger thickness were employed (Section 3.3, Table 1). This effect is due to the non-uniform radical concentration which arises when the depth of penetration of the photolyzing light becomes too short. The effect can be corrected by use of the model detailed in Section 3.3. The corrected rate constant for the self-termination of the radical is $2k = (6 \pm 1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in propanol(-2) at 12°C.

When air-saturated solutions were photolyzed, the N-hydropyridinyl radical decay was of first order, $k = 1.8 \cdot 10^3 \text{ s}^{-1}$ at 12°C. The first-order rate constant became successively smaller upon purging the solution with nitrogen, and the rate law gradually changed until it became second-order when the oxygen content of the solution was small enough. In the air-saturated solution, O₂ attains a constant steady-state concentration during the intermittent photolysis which is at least one order of magnitude smaller than the saturation concentration. Since we are not yet able to measure the steady-state concentration of O₂ in the photolysis zone, we can only estimate a lower limit of the rate constant, k_{O_2} , for the reaction of the N-hydropyridinyl radical with oxygen. Taking $c_{O_2} < 2 \cdot 10^{-4}$ M in the photolyzed volume (typical values of the saturation concentration of O₂ in various alcohols are ca. $2 \cdot 10^{-3}$ M [16]), we estimate $k_{O_2} > 10^7$ M⁻¹ s⁻¹.

3.3. Influence of Non-Uniform Radical Concentration on the Apparent Second-Order Rate Constant

While non-uniform radical concentration does not influence the first-order rate constant as measured by time-resolved ESR, the related problem for the second-order reaction has been of concern for many authors. (See, e.g., the literature cited in Ref. [12].) In the following, we present a scheme how to correct this influence for the case of the second-order self-reaction of a radical which is formed directly from the excited state of a light-absorbing parent compound in solution [11].

Fig. 5 shows the cross-section of the ESR flat cell (thickness, d) along the direction, x, of the photolyzing light (monochromatic; intensity I_0 at x = 0). If the local radical concentration, R(x, y, z, t), were exactly uniform, the familiar relation,

$$\bar{R}/R(t) = 2k \cdot \bar{R} \cdot t + 1 \tag{1}$$

would hold for the second-order decay of the radical concentration, R(t), observed when the light is switched off at time t = 0. \overline{R} denotes the uniform initial concentration as established during the light period.



Cross-sectional view of the photolysis zone in the ESR flat cell. The z-direction coincides with the sample axis of the rectangular microwave cavity. R(x, y, z, t): time-dependent local radical concentration; u_z : z-component of the velocity of flow; d: thickness of the cell in the direction, x, of the photolysis light

The slope, $m = 2k \cdot \overline{R}$, of the linear plot, Eq. (1), gives the desired rate constant, 2k, since \overline{R} is a measurable quantity. (See, e.g., Fig. 2.) This is an idealized situation, however, since the absorption of light (Lambert-Beer law) necessarily induces a non-uniformity of the radical concentration along the direction of the light beam. The problem is how to optimize the experimental conditions for maximum allowable absorption of light (i.e., for efficient radical production) while, simultaneously, keeping the systematic error in 2k to be expected because of non-uniform radical concentration reasonably small.

The complete rate equation for the local radical concentration, R(x, y, z, t), is

$$\partial R / \partial t = p + r + D_{\rm R} \,\nabla^2 R + \mathbf{u} \cdot \nabla R \,. \tag{2}$$

p(x, y, z, t) and r(x, y, z, t) are the local rate of radical production by photolysis and of chemical radical reactions, respectively. The remaining terms account for changes in R by diffusional and convective transport (D_R , diffusion coefficient of the radical; **u**, linear velocity of flow of the solution). For the present purpose we assume, firstly, that the radical is formed directly from the excited state of the parent (concentration independent of space and time) and, secondly, that the radical undergoes a second-order irreversible self-reaction. Under our conditions, the transport terms can be neglected and non-uniformity of p and r occurs in the x-direction only. Eq. (2) then reads

$$\partial R(x,t)/\partial t = 2.303 \varepsilon \phi I_0 A \exp(-2.303 \varepsilon A x) - 2k \cdot R^2(x,t).$$
(3)

 ε is the molar extinction coefficient of the parent to be photolyzed, ϕ is the quantum yield of radical production, I_0 is the intensity at x = 0 of the monochromatic photolysis light, and A is the concentration of the parent compound.

For the following, it should be noted that the ESR spectrometer does not monitor the local radical concentration but rather averages the local concentration over the volume of the photolysis zone,

$$\langle R(t) \rangle = d^{-1} \cdot \int_{0}^{d} R(x, t) \, \mathrm{d}x \,.$$
 (4)

In the steady state of photolysis, $\partial R/\partial t = 0$, the spectrometer measures the steady-state value, $\langle \bar{R} \rangle$, of the quantity $\langle R(t) \rangle$ which is obtained from Eq. (3) by use of Eq. (4) and is given by

$$\langle \bar{R} \rangle = R(0) \cdot 2\delta \cdot [1 - \exp(-1/2\delta)].$$
(5)

R(0) is the local radical concentration at x = 0 and δ denotes the relative depth of penetration of the photolysis light,

$$\delta = (2.303 \cdot \varepsilon \cdot A \cdot d)^{-1} \,. \tag{6}$$

(Note, that δ refers to the thickness, d, of the ESR cell and that for exactly uniform radical concentration $\delta \to \infty$ would be required.)



Calculated decay of the spatially averaged radical concentration $\langle R \rangle / \langle \bar{R} \rangle$ as a function of time for various values of the relative penetration depth δ . Dimensionless representation using the spatially averaged steady state concentration $\langle \bar{R} \rangle$ and the first half-life $t_{1/2}(0)$ at x = 0 of the radical



Second-order plot of the curves shown in Fig. 6. The broken line has been calculated for the same initial number of radicals present as with $\delta = 0.1$, however distributed uniformly over the photolysis volume

The decay of the ESR signal in the dark period is given by

$$\langle R(\theta) \rangle = \frac{R(0)2\delta}{\theta} \ln \left(\frac{\theta + 1}{\theta \cdot \exp(-1/2\delta) + 1} \right).$$
(7)

 θ stands for the dimensionless variable, $t/t_{1/2}(0)$, where $t_{1/2}(0)$ is the first half-life of the radical in the solution at x = 0. Fig. 6 shows the function, Eq. (7), in dimensionless co-ordinates, where $\langle R(\theta) \rangle$ has been normalized to the steady-state concentration, $\langle \overline{R} \rangle = \langle R(\theta = 0) \rangle$, Eq. (5). While the curves in Fig. 6 do not depend on 2k, they do depend

on the relative penetration depth, δ . These curves correspond to the decay of the ESR signal as monitored by the spectrometer. If, as usual, these curves are evaluated in terms of a second-order plot, $\langle R \rangle / \langle R \rangle$ vs. time, we obtain the representation shown in Fig. 7. For uniform radical concentration, the usual straight line is obtained. For finite penetration depth the function exhibits a slight deviation from linearity and the curvature increases with decreasing values of δ . Also shown in Fig. 7 (broken line) is the situation expected when the same number of radicals present in the steady state of the photolysis with $\delta = 0.1$ were distributed uniformly over the cell volume. In this case again the familiar straight line is obtained. However, the slope is smaller than for the curve calculated for $\delta = 0.1$. (This is due to the fact that the first half-life of the radical has become longer, since R(0) is correspondingly smaller in the hypothetical case of uniform distribution of a given number of radicals.) Inspection of all the curves calculated for various values of δ indicates that the deviation from linearity in the useful range of a typical ESR decay curve, say $0 < t/t_{1/2}(0) < 10$, is so small that the approximation by a linear function is justified in each case. While for uniform radical concentration the rate constant from the second-order plot, $1/\langle R(t) \rangle$ vs. t is $2k = m/\bar{R}$, Eq. (1), the same rate constant is given by

$$2k \approx m^* \cdot f/\langle \bar{R} \rangle \tag{8}$$

in the general case of non-uniform radical concentration. Here, m^* is the slope of the virtually linear experimental second-order plot $(1/\langle R(t) \rangle \text{ vs. } t), \langle \overline{R} \rangle$ is the spatial average of the radical concentration measured in the steady state before switching off the light at t = 0, and $f = f(\delta)$ is a correction factor obtainable by comparison of the slopes of the $1/\langle R(t) \rangle$ vs. t curves as calculated for uniform and non-uniform radical concentration, however for the same number of radicals present in both cases. Fig. 8 shows the correction factor as a function of the relative depth of penetration, δ , of the photolysis light. It is seen that for $\delta \ge 1/3$ the factor f is virtually unity. For $\delta = 1/3$, ca. 95% of the light is used for the photolysis of the parent compound and the correction factor, f = 0.97, still can be neglected for almost all measurements. We therefore consider $\delta = 1/3$ the optimum for kinetic ESR studies of photochemical radical reactions which obey the above mechanism.



Plot of the correction factor f as a function of the relative depth of penetration of the photolysis light, δ . (See Eqs. (6) and (8) for definition of δ and f, respectively)

Table 1 summarizes some results for the photolysis of pyridine in propanol(-2) where the relative penetration depth has been varied by using different concentrations of pyridine and flat cells of different thickness. As seen, the apparent values, $2k^*$, of the rate constant obtained from the non-corrected plot, $1/\langle R \rangle$ vs. *t*, increase drastically with decreasing values of δ . (This is mainly due to the erroneous determination of concentration which tacitly assumes uniform distribution of radicals even when the production of radicals is confined to a thin layer next to the front wall of the cell.) The values of $2k^*$ can, however, be corrected to give the true rate constant, 2k, when use is made of the function $f(\delta)$ in Fig. 8.

Basu and McLauchlan considered the related problem for the case of flash photolysis in conjunction with time-resolved ESR [12]. Although

of the N-hydropyndinyl radical in propulsi (2)					
c/Mª)	d/mm ^b)	δ°)	f ^d)	$2k^*/M^{-1}s^{-1}$	$2k/M^{-1}s^{-1}$
1.24	0.5	0.035	0.22	28 · 10 ⁸	6.2 · 10 ⁸
1.24	0.2	0.088	0.55	$10 \cdot 10^8$	5.5 · 108
0.12	0.5	0,35	0.98	5.0 · 108	4.9 · 10 ⁸
0.12	0.2	0.88	1.00	6.8 · 10 ⁸	6.8 · 10 ⁸

Table 1 Apparent $(2k^*)$ and true values (2k) of the self-termination rate constant at $12^{\circ}C$ of the N-hydropyridinyl radical in propanol(-2)

a) Concentration of pyridine in propanol(-2).

b) Thickness of the ESR flat cell along the direction of the photolysis light.

c) Relative depth of penetration of light, Eq. (6), with $\varepsilon = 200 \, l \cdot mol^{-1} \cdot cm^{-1}$ at 270 nm.

d) Correction factor, Fig. 8.

they used essentially the same model as presented here, they set much narrower bounds to the minimum allowable value of the penetration depth. We believe that their conclusion has to be revised by taking into account the number of radicals produced in photolytic experiments performed with different values of the penetration depth.

4. Discussion

We cannot yet distinguish between the two possible self-termination reactions of the radical. These are self-combination to give dihydropyridine dimers and/or disproportionation to give pyridine and dihydropyridine isomers. In fact all these molecules are unstable [17] and tend to react further, e.g., by solvolysis, which ultimately leads to the destruction of the pyridine ring. It is therefore understandable that our attempt to isolate, by thin-layer chromatography, the primary products of the selftermination reaction failed. Polymeric products were present only which could not be characterized.

The rate constant measured in propanol(-2)/acetone containing 50% (by volume) of water is very close to the value of $2k = 8 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ reported by Cercek and Ebert for the 275 nm transient observed during pulse radiolysis of aqueous solutions of pyridine [6]. This transient was singled out by computer simulation of a complex reaction scheme and was tentatively ascribed to the N-hydropyridinyl radical. Our present result lends strong support to this interpretation. Further, our finding of pH-independence of the termination rate constant of the N-hydropyridinyl radical favors the assumption that the self-reaction is combination rather than disproportionation.

All the measurements made in propanol(-2)/acetone indicate that the self-termination is not diffusion controlled in this solvent. In parallel to our previous results on the self-reaction kinetics of the N-hydro-4-acetylpyridinyl radical [1], we find that both the activation energy and the frequency factor of the self-termination in propanol(-2)/acetone (1:1) are smaller than the respective values for the diffusional encounter of radicals in this solvent. As discussed earlier [1], this can be explained by a mechanism which consists of two consecutive reactions, the reversible formation of a charge-transfer type dimeric radical complex followed by the irreversible formation of the σ -bonded radical dimer (or of the products of radical disproportionation). Our observation of the correlation between the termination rate constant and the solvent polarity parameter Z in aqueous propanol(-2)/acetone mixtures (Fig. 4) may be taken as additional support of such a mechanism. This latter argument should not be overestimated, however. Kosower's Z-value for propanol(-2) is 76.3 at 25 °C [13], yet the termination rate constant measured in propanol(-2) is appreciably larger than expected from the correlation line of Fig. 4. Hence, specific radical-solvent interaction may influence the rate constant.

Other than in propanol(-2)/acetone (1:1) the termination rate constant, 2k, in neat propanol(-2) at 12°C agrees with the value, $2k_d$, expected for diffusion control. From Eq. (3) of our previous work [1] we obtain $2k_d = 5 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 12°C. 2k from the present work is $(6 \pm 1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

We do not know whether the reaction of the N-hydropyridinyl radical with dissolved oxygen in propanol(-2), $k_{O_2} > 10^7$ M⁻¹ s⁻¹ at 12°C, leads to reoxidation to give pyridine or rather to the formation of an O₂-adduct radical (peroxyradical). Product studies have not been made in this case.

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