

THE 1-HYDRO-2,6-DIMETHYL-3,5-DICYANOPYRIDINYL RADICAL IN SOLUTION: MECHANISMS OF PHOTOCHEMICAL FORMATION AND KINETICS OF DISAPPEARANCE BY SELF-COMBINATION

R. LEUSCHNER[†] and J. K. DOHRMANN

Institut für Physikalische Chemie der Freien Universität Berlin, Takustrasse 3, D-1000 Berlin 33 (F.R.G.)

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Summary

The 1-hydro-2,6-dimethyl-3,5-dicyanopyridinyl radical (HDCP·) has been identified by electron spin resonance spectroscopy (ESR) in solution at room temperature as an intermediate during both the 280 - 300 nm photoreduction of 2,6-dimethyl-3,5-dicyanopyridine (DCP) in 2-propanol and the 270 - 300 nm photo-oxidation of the corresponding 1,4-dihydropyridine (H₂DCP) in oxygenated aqueous acetone. The hyperfine couplings and the *g* value of HDCP· are reported. The rate constant for the second-order self-combination of HDCP· as determined by time-resolved ESR is $2k = (1.6 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in 2-propanol at 20 °C. In addition to the HDCP· radical dimer (yield, 24%), combination products of the (CH₃)₂ĊOH and the HDCP· radicals (total yield, 32%) have been identified among the products of the photoreduction of DCP in 2-propanol. Also reported are the quantum yields of DCP disappearance (0.07 and 0.15 at 280 nm and 300 nm respectively) and fluorescence quenching studies of aqueous solutions of DCP in the presence of 2-propanol. The various results are rationalized in terms of a mechanism proposed for the photoreduction of DCP in 2-propanol. It is suggested that the radical and product formation originates from the lowest excited ¹(n-π*) state of DCP. The formation of the HDCP· radical by photo-oxidation of H₂DCP in oxygenated aqueous acetone is thought to proceed via singlet oxygen.

1. Introduction

The redox chemistry of pyridines substituted with electronegative groups in the 3-position or the 3- and 5-positions is of fundamental interest since these molecules are analogous with the NAD⁺/NADH couple (NAD⁺, nicotinamide adenine dinucleotide; NADH, dihydronicotinamide adenine dinucleotide), which is important for many biochemical redox processes.

[†]Present address: Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.

Reduction of pyridine compounds to give the corresponding pyridinyl radicals has been proven by electron spin resonance spectroscopy (ESR) in solution during the photolysis of several 3-substituted pyridines, including nicotinamide [1, 2]. These radicals represent the oxidation state that is intermediate between those of the pyridine (oxidized form) and the dehydropyridine (two-electron reduced form). (For a review on nicotinamidinyl adenine dinucleotide (NAD \cdot) and nicotinamidinyl adenine dinucleotide phosphate (NADP \cdot) radicals, see ref. 3.)

In the present paper we demonstrate by *in situ* ESR that the 1-hydro-2,6-dimethyl-3,5-dicyanopyridinyl radical (HDCP \cdot), which is very short lived in solution, can be generated both by photoreduction of the corresponding pyridine (DCP) and by photo-oxidation of the 1,4-dihydropyridine (H₂DCP) (see Fig. 1).

The product studies and measurements of quantum yields for the photoreduction reaction, together with the value of the termination rate constant of the radical, strongly suggest that the HDCP \cdot radical is formed from a singlet excited state of DCP rather than from a triplet state. Also reported are observations by ESR which may be taken to indicate formation of HDCP \cdot via singlet oxygen during the photo-oxidation of H₂DCP.

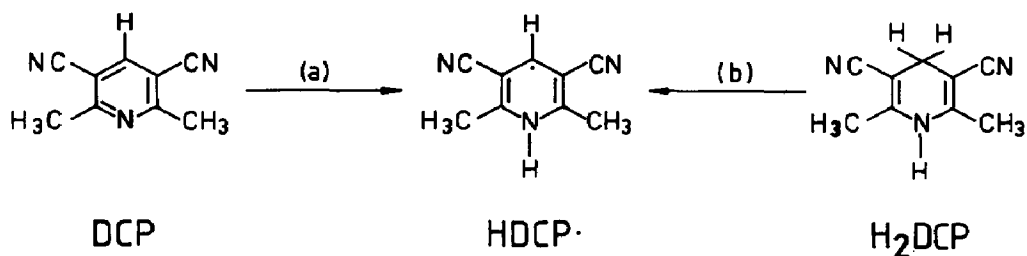


Fig. 1. Generation of HDCP \cdot radical: (a) 280 - 300 nm (2-propanol-acetone); (b) 270 - 300 nm (water-acetone-O₂).

2. Experimental details

Our technique of performing ESR measurements during continuous [4] and intermittent [5] photolysis of liquid solutions has been described previously. In the present case, solutions of DCP or H₂DCP were photolysed near 280 - 300 nm while slowly flowing through a flat quartz cell (width, 10 mm; optical path, 0.5 mm) located inside the dual cavity of the Varian E-9 ESR spectrometer. The rotating sector method was used for the time-resolved ESR studies. These were performed on the hyperfine line marked with an asterisk in Fig. 2 (the spectrum of HDCP \cdot was obtained during the photoreduction of DCP). The radical concentration was measured by ESR as described previously [5].

Product studies were performed for solutions of DCP in 2-propanol after photolysis (quartz cell; optical path, 30 mm) using filtered light from a 1 kW Xe-Hg high pressure lamp (Hanovia 977 B 1, aqueous NiSO₄ and CoSO₄ solutions, Schott filter UG 5). The various products were separated

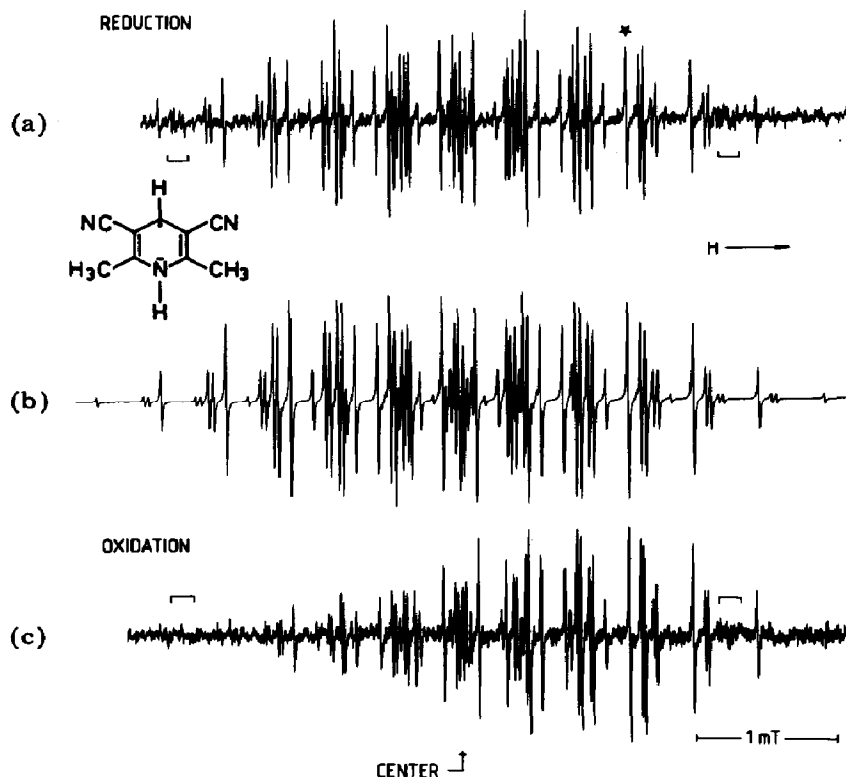


Fig. 2. Experimental ESR spectra of $\text{HDCP}\cdot$ in solution at about 20°C during the 280 - 300 nm photolysis of (a) 0.03 M DCP in 2-propanol and of (c) 5 mM H_2DCP in water-acetone (1/1 v/v) saturated with air under atmospheric pressure. The brackets indicate lines from $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and the asterisk denotes the line used for time-resolved ESR. (b) is a simulated ESR spectrum.

by thin-layer chromatography (Al_2O_3 60 F 254 from Merck; *n*-hexane-ethyl acetate (1/1 v/v)) and were analysed by UV-visible absorption spectrophotometry (Zeiss DMR 22) in 2-propanol solution as well as by mass spectrometry. For the determination of the quantum yield of disappearance of DCP, additional interference filters were used to isolate the 279 and 299 nm wavelengths (Schott UV-IL 279 and UV-I 299). The photon flux was measured by actinometry using potassium ferrioxalate [6]. Fluorescence spectra were recorded using a Perkin-Elmer MPF-44 B spectrophotometer. The solutions to be studied were carefully freed of dissolved oxygen by purging with purified nitrogen gas. All measurements were made at about 20°C .

1,4-Dihydro-2,6-dimethyl-3,5-dicyanopyridine (H_2DCP) was prepared according to the procedure of Lukeš and Kuthan [7] (melting point, 219°C , after recrystallization from 0.1 M HCl-methanol). 2,6-Dimethyl-3,5-dicyanopyridine (melting point, 119°C , after purification by sublimation) was obtained from H_2DCP by oxidation with HNO_2 . Reagent grade 2-propanol and acetone were used as purchased from Merck. 2-Propanol (Merck Uvasol) was used for the fluorescence studies.

3. Results and discussion

3.1. Generation and electron spin resonance study of the HDCP· radical

3.1.1. Photoreduction of DCP

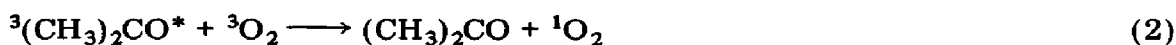
The UV-visible spectrum of DCP in 2-propanol exhibits a strong absorption band at 279 nm ($\pi-\pi^*$, $\epsilon = 3700 \text{ M}^{-1} \text{ cm}^{-1}$) which superimposes a much weaker band ($n-\pi^*$) located at about 300 nm. During the 280 nm photolysis (Schott filter UV-R, bandwidth ± 50 nm) of a 0.03 M solution of DCP in 2-propanol the ESR spectrum of the HDCP· radical was identified (Fig. 2(a)). The radical concentration was about 8×10^{-7} M and could be increased by about 40% when acetone (20 vol.%) was added to the solution. The increase is attributed to the production of additional $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals which can reduce ground state DCP.

Analysis of the hyperfine structure, and corroboration by simulation of the spectrum (Fig. 2(b)), leads to the following values for the couplings: 0.378 mT (ring nitrogen), 0.343 mT (NH proton), 1.339 mT (CH proton in the 4-position) and 0.468 mT (six equivalent CH_3 protons). The g value is 2.00271. As expected from our previous ESR studies, *e.g.* see refs. 2 and 8, the position with the largest π -spin population ($\rho^\pi = 0.46$) is the carbon para to the ring nitrogen. The small value of the nitrogen coupling is surprising, when compared with the 1-hydro-2,6-dimethylpyridinyl radical [9]. No splittings could be resolved from the CN nitrogen atoms. We conclude that the coupling is smaller than the line width of 0.01 mT. The coupling is thus even smaller than the value of 0.023 mT measured previously for the CN nitrogen in the related 1-hydro-3-cyanopyridinyl radical [2].

3.1.2. Photo-oxidation of H_2DCP

An ESR spectrum (Fig. 2(c)) of the HDCP· radical was also obtained during the 270 - 300 nm photolysis of an air-saturated solution of H_2DCP (5 mM) in water-acetone (1:1 by volume). Except for the differences in height of corresponding high and low field lines (chemically induced dynamic electron polarization (CIDEP) effect) and small solvent-induced changes in the couplings, the spectrum was identical with that shown in Fig. 2(a). Experiments using appropriate filters revealed that the radical generation required the excitation of acetone ($\lambda_{\text{max}} = 270$ nm; $\epsilon = 16 \text{ M}^{-1} \text{ cm}^{-1}$), whereas the excitation of H_2DCP alone ($\lambda_{\text{max}} = 345$ nm; $\epsilon = 5300 \text{ M}^{-1} \text{ cm}^{-1}$) did not produce the radical. In oxygen-free solution the ESR signal was much weaker.

The enhancement of the ESR signal in air-saturated solution may be understood by assuming that singlet oxygen formed by energy transfer from triplet acetone to $^3\text{O}_2$ acts as an oxidizing agent to give HDCP· from H_2DCP (see Scheme 1). An analogous mechanism has been reported for NADH [10]. Hydrogen abstraction from H_2DCP by triplet acetone is obviously an additional but less efficient route of radical formation. It has been pointed out that pyridinyl radicals are normally not observable during the oxidation of dihydropyridines owing to the ease of further oxidation to pyridines [11].



Scheme 1.

As for the chemical lifetime of HDCP· in the steady state photolysis, the obvious difference between the photoreduction and photo-oxidation process is that in the latter there is a second sink (reaction (4)) for the disappearance of HDCP·, in addition to the self-reaction (reaction (5)), which operates in both cases (see Section 3.2). Land and Swallow reported $k_4 = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation by ${}^3\text{O}_2$ of the NAD· radical in aqueous solution [12]. The lifetime of HDCP· must, therefore, be shorter in the presence than in the absence of ${}^3\text{O}_2$. This may be one of the reasons why the CIDEP effect was seen only in spectrum (c) of Fig. 2. The intensity distortions (enhanced absorption in the high field portion and emissive components in the low field portion of the spectrum) suggest that the CIDEP effect stems from the radical-pair mechanism [13].

3.2. Termination kinetics of the HDCP· radical studied by time-resolved electron spin resonance spectroscopy

The second-order rate constant ($2k_5$ in Scheme 1) for the self-reaction of HDCP· has been determined by time-resolved ESR during intermittent photolysis of 0.01 M and 0.1 M solutions of DCP in 2-propanol and 2-propanol-acetone (4:1 by volume) respectively. Figure 3 shows a representative example of such a measurement. The values of $2k_5$ obtained from the decay curves in the dark period are $(1.6 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$

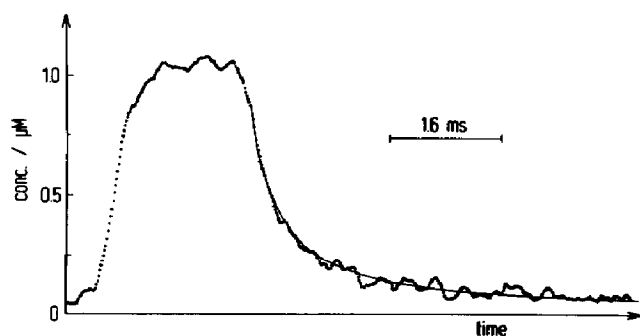
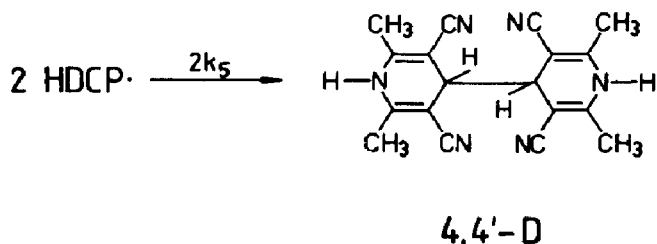


Fig. 3. Concentration of the radical HDCP· as a function of time during intermittent photolysis of DCP in 2-propanol-acetone (20 vol.%) at 20 °C (average of 48 000 transients) and calculated decay curve for second-order self-reaction of HDCP· in the dark period ($2k_5 = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

(2-propanol, 20 °C) and $(2.7 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (2-propanol-acetone, 20 °C). Comparison of these rate constants with the values calculated by the Stokes-Einstein-Smoluchowsky equation [14], including a spin statistical factor of 1/4 for the self-reaction of singlet pairs, indicates that the reaction is diffusion controlled. From the product studies reported in Section 3.3 we conclude that the self-reaction is a combination of two radicals to give C-C dimers, mainly 4,4'-D:

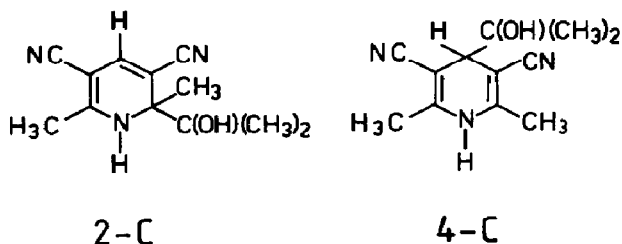


This is reasonable since the 4-position is unsubstituted and carries the largest fraction ($\rho_4^\pi = 0.46$) of the unpaired electron.

It should be noted here that the self-reaction of HDCP· is the fastest one hitherto reported for electroneutral 1-hydroxypyridinyl radicals. The value of $2k_5$ for the unsubstituted radical ($\rho_4^\pi = 0.39$) in 2-propanol-acetone (1:1 by volume) is $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C although the viscosity of this solvent mixture is even lower [15].

3.3. Product studies: photoreduction of DCP in 2-propanol

0.02 M solutions of DCP in 2-propanol were photolysed to give a conversion of DCP up to 60%. After separation by thin-layer chromatography, the products 2-C and 4-C



were amongst those which could be characterized by spectrophotometry and mass spectrometry: 2-C ($\lambda_{\text{max}} \approx 380 \text{ nm}$; $m/z = 217$); 4-C ($\lambda_{\text{max}} \approx 345 \text{ nm}$; $m/z = 217$); 4,4'-D ($\lambda_{\text{max}} = 348 \text{ nm}$; $m/z = 317$; melting point, above 300 °C); 1,4-H₂DCP ($\lambda_{\text{max}} = 345 \text{ nm}$). These compounds were not all the products actually formed. The remainder could not be separated by thin-layer chromatography. From spectrophotometry, pyridine and dihydropyridine derivatives can be excluded. The structure assigned to 2-C and 4-C is based on a comparison of the λ_{max} with the values of 375 nm and 345 nm reported for 1,2-H₂DCP and 1,4-H₂DCP respectively [16].

The yield of product P, $y(\text{P}) = -\nu_p \Delta c(\text{P}) / \Delta c(\text{DCP})$, was determined by spectrophotometry, where $\epsilon = 5300 \text{ M}^{-1} \text{ cm}^{-1}$ (molar extinction coefficient

of 1,4-H₂DCP at 345 nm) was taken to be valid for all products containing the dihydropyridine moiety. (The stoichiometric numbers $\nu_p = 2$ for 4,4'-D and $\nu_p = 1$ for the monomeric products were taken into account.) The following yields were obtained: $y(2-C + 4-C) = 0.32$, $y(4,4'-D) = 0.24$ and $y(1,4-H_2DCP) = 0.02$. It is seen that the cross-combination products 2-C and 4-C of the HDCP· and the (CH₃)₂ĊOH radical (from the solvent) outweigh the self-combination product of HDCP·, although the steady state ESR spectra clearly show that the concentration of free HDCP· radicals is much larger than that of (CH₃)₂ĊOH radicals (Fig. 2(a)). Since the separation of the 2-C and 4-C isomers was incomplete, only the sum of the yields of both isomers could be determined. There is evidence, however, that 4-C constitutes the main portion of the two isomers.

Also measured was the quantum yield ϕ_{-DCP} of disappearance of DCP, at 280 ± 5 and 300 ± 5 nm. In 2-propanol with 0.15 mM DCP, the quantum yields are $\phi_{-DCP} = 0.07$ (280 nm) and $\phi_{-DCP} = 0.15$ (300 nm). In these experiments, the change in the concentration of DCP was measured spectrophotometrically at 279 nm after different photolysis times. Figure 4 shows a representative example.

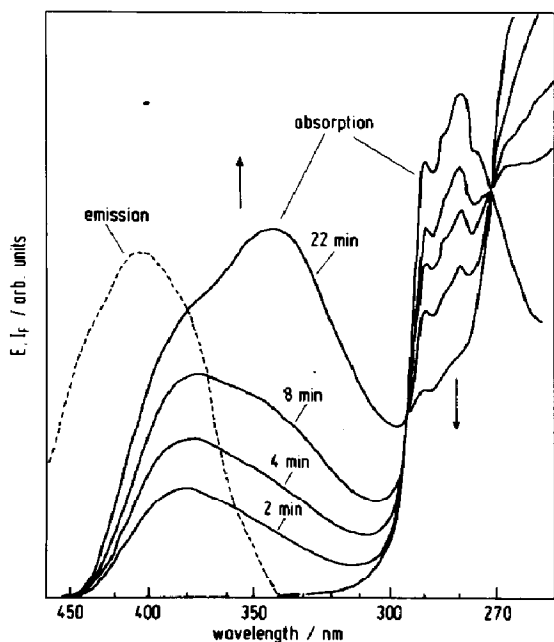


Fig. 4. Absorption spectra before and after 280 nm photolysis of 0.15 mM DCP in 2-propanol at room temperature. (Absorption bands emerging near 340 and 380 nm are from products with dihydropyridine structure.) — — —, fluorescence spectrum of 0.3 mM DCP in water (unphotolysed, 280 nm excitation).

3.4. Fluorescence studies

The large yield of the products 2-C and 4-C obtained on the photo-reduction of DCP as well as the ESR spectra which indicate that 2-C and

4-C are probably not formed by cross-combination of free HDCP· and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals strongly suggest that a singlet excited state of DCP rather than a triplet state is the precursor of the photoproducts. Fluorescence spectra were therefore taken on 280 nm excitation of DCP (0.3 mM) in water and in the presence of various amounts of 2-propanol. In the absence of 2-propanol, a weak fluorescence ($\lambda_{\text{max}} = 410$ nm) was seen (Fig. 4). Neither the vibrational structure of the $^1(\pi-\pi^*)$ absorption band centred at 280 nm nor the usual mirror relation between emission and absorption were found for the fluorescence band of DCP. This indicates that the fluorescence is not from the $^1(\pi-\pi^*)$ state (S_2) but is rather from the lower lying $^1(n-\pi^*)$ state (S_1) of DCP (see Scheme 2). Upon addition of 2-propanol the fluorescence intensity decreased. Figure 5 shows the Stern-Volmer plot of the relative fluorescence quantum yield

$$\phi_F^0/\phi_F^{\text{ROH}} = 1 + t_s k_Q [\text{ROH}]$$

ϕ_F^0 and ϕ_F^{ROH} denote the quantum yield in water and in the presence of 2-propanol respectively. From the straight line in Fig. 5 we obtain $t_s k_Q = 0.09 \pm 0.01 \text{ M}^{-1}$ for the product of the mean life t_s of the fluorescing singlet state with the quenching rate constant k_Q .

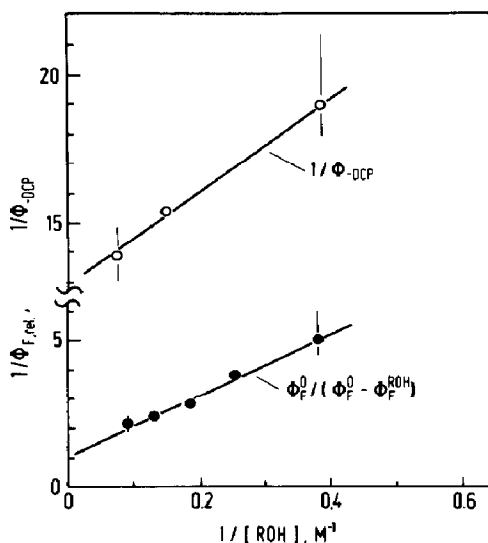
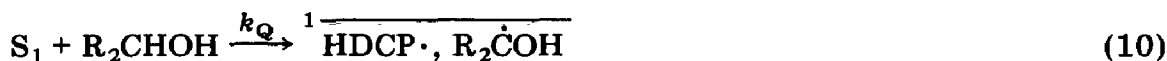
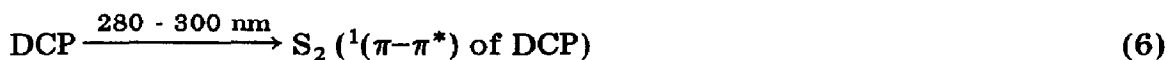


Fig. 5. Reciprocal values of the quantum yield ϕ_{DCP} for disappearance of DCP at 280 nm and of the relative fluorescence quantum yield $1 - (\phi_F^{\text{ROH}}/\phi_F^0)$ during 280 nm excitation vs. reciprocal concentration of 2-propanol in an aqueous solution of DCP at room temperature. ϕ_F^{ROH} and ϕ_F^0 are the fluorescence quantum yields in 2-propanol-water and water respectively.

3.5. Proposed mechanism of HDCP· radical and product formation during the 280 - 300 nm photolysis of DCP in 2-propanol

In an attempt to account for the above findings we suggest the mechanism given in Scheme 2.



Scheme 2.

From the ESR and product studies, at least 60% of the photochemistry of DCP proceeds via the HDCP· radical formed by hydrogen-atom addition from $(\text{CH}_3)_2\text{CHOH}$ to the ring nitrogen. This requires that the photochemically active state has $n-\pi^*$ character [17]. The active state is obviously not from the triplet manifold of DCP. Reaction from a triplet state would yield free radicals, HDCP· and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, which would escape from the solvent-

encaged triplet radical pair ($\overset{3}{\text{HDCP}\cdot, \text{R}_2\dot{\text{C}}\text{OH}}$). Since $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ can reduce ground-state DCP (reaction (13)), a much higher yield of 4,4'-D would be expected from the diffusion-controlled self-combination of HDCP· (reaction (14)). Such a mechanism has been found previously for the photoreduction of 4-acetylpyridine in 2-propanol [18] and, similarly, for 4-cyanopyridine (work in progress in this laboratory). In the present case, the yield of 4,4'-D is even smaller than that of 4-C and 2-C. These latter products must be

derived mostly from the singlet radical pair $\overset{1}{\text{HDCP}\cdot, \text{R}_2\dot{\text{C}}\text{OH}}$ (reaction (11), which in turn stems from the $^1(n-\pi^*)$ state of DCP. Only those radicals which have escaped from the solvent-encaged singlet pair (reaction (12)) with $k_{esc} < k_c$ can contribute to the formation of 4,4'-D. (Only these radicals give rise to the observed ESR spectrum.)

The fluorescence studies indicate that the photochemically active $^1(n-\pi^*)$ state of DCP (S_1 in Scheme 2) is energetically lower than the initially

populated $^1(\pi-\pi^*)$ state (S_2). Depopulation of S_2 to give the $^3(n-\pi^*)$ state (T_2) by intersystem crossing (ISC) (reaction (7)) is expected to be efficient, since the triplet quantum yield of the related molecule 3-cyanopyridine is about 0.8 [19]. Since no photochemistry originating from the $^3(n-\pi^*)$ state (T_2) has been found, it is tempting to postulate a lower lying $^3(\pi-\pi^*)$ state (T_1) of DCP, which is inactive in the radical formation process. This would again parallel the properties of 3-cyanopyridine whose lowest triplet state has $\pi-\pi^*$ character [19]. An efficient ISC (reaction (7)) would also explain the small value of the quantum yield $\phi_{-DCP}(280 \text{ nm}) = 0.07$. The competing formation of the photochemically active S_1 state by the $S_2(\pi-\pi^*)$ to $S_1(n-\pi^*)$ transition (reaction (8)) requires a coupling mechanism. As discussed previously by Testa and Wild [20] and also by van Bergen and Kellogg [21], vibronic coupling between the S_1 and S_2 states would enhance such a transition. The vibrational structure of the $^1(\pi-\pi^*)$ absorption band of DCP (Fig. 4) corresponds to an energy of 600 cm^{-1} and can be assigned to an out-of-plane vibration of the S_2 state [22], which could couple with the S_1 state. The $n-\pi^*$ character of the S_1 state of DCP parallels that of the lowest excited singlet state of 3-cyanopyridine [19].

The fluorescence studies reported above also afford an estimate of the quantum yield ϕ_{T_2} for S_2 to T_2 ISC (reaction (7)). Extrapolation of the straight line in the Stern-Volmer plot (Fig. 5) to the value (13 M) of the 2-propanol concentration in neat 2-propanol gives $\phi_F^{\text{ROH}}/\phi_F^0 = 0.46$. This indicates that about 50% of the DCP molecules in the S_1 state react in neat 2-propanol, while the remainder relaxes by fluorescence, thermal deactivation or S_1 to T_1 ISC. From Scheme 2, the quantum yield ϕ_{S_1} for the formation of S_1 molecules via the S_2 state (280 nm excitation of DCP) can be derived: $\phi_{S_1} = \{1 - (\phi_F^{\text{ROH}}/\phi_F^0)\}^{-1} \phi_{-DCP}$. Taking $\phi_{-DCP} = 0.07$ as determined for the 280 nm photolysis of DCP in 2-propanol, we obtain $\phi_{S_1} = 0.13$ and $\phi_{T_2} = 1 - \phi_{S_1} = 0.87$. The value of 0.87 is close to the triplet quantum yield of about 0.8 reported for 3-cyanopyridine [19]. (In this estimate we neglect the possible formation of Dewar-DCP which might derive from the S_2 state. Dewar-pyridines have been found in photoreactions of other 3,5-substituted pyridines [21] and of pyridine itself [23]; however, the quantum yield is very small [23].) On 300 nm photolysis, a larger quantum yield ($\phi_{-DCP} = 0.15$) was found for the disappearance of DCP. 300 nm light excites transitions of ground state DCP to both the S_1 and the S_2 state. This explains why ϕ_{-DCP} is larger at 300 nm than at 280 nm.

In a previous investigation of the photochemistry of some esters of pyridine-3,5-dicarboxylic acid, mostly products from the cross-combination (and disproportionation) reactions of the corresponding 1-hydropyridinyl radical and the counter radical from the alcoholic solvent have been found [21]. Obviously, the photochemistry of DCP in 2-propanol is quite similar.

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