JOC Article

Generation and Reactivity of Ketyl Radicals with Lignin Related Structures. On the Importance of the Ketyl Pathway in the Photoyellowing of Lignin Containing Pulps and Papers

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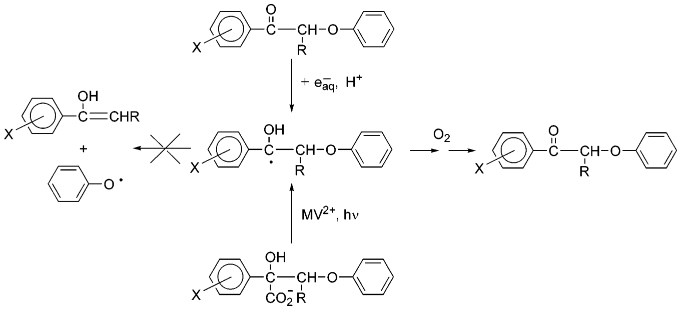

Ketyl radicals with lignin related structures have been generated by means of radiation chemical and photochemical techniques. In the former studies ketyl radicals are produced by reaction of α-carbonyl-β-aryl ether lignin models with the solvated electron produced by pulse radiolysis of an aqueous solution at pH 6.0. The UV−vis spectra of ketyl radicals are characterized by three main absorption bands. The shape and position of these bands slightly change when the spectra are recorded in alkaline solution (pH 11.0) being now assigned to the ketyl radical anions and a $pK_a = 9.5$ is determined for the 1-(3,4,5-trimethoxyphenyl)-2-phenoxyethanol-1-yl radical. Decay rates of ketyl radicals are found to be dose dependent and, at low doses, lie in the range $(1.7-2.7) \times 10^3$ s^{-1}. In the presence of oxygen a fast decay of the ketyl radicals is observed ($k_2 = 1.8-2.7 \times 10^9$ M^{-1} s^{-1}) that is accompanied by the formation of stable products, i.e., the starting ketones. In the photochemical studies ketyl radicals have been produced by charge-transfer (CT) photoactivation of the electron donor−acceptor salts of methyl viologen (MV^{2+}) with α-hydroxy-α-phenoxymethyl-aryl acetates. This process leads to the instantaneous formation of the reduced acceptor (methyl viologen radical cation, $MV^{+\bullet}$), as is clearly shown in a laser flash photolysis experiment by the two absorption bands centered at 390 and 605 nm, and an acyloxyl radical [$ArC(CO_2^\bullet)(OH)CH_2$-$(OC_6H_5)$], which undergoes a very fast decarboxylation with formation of the ketyl radicals. Steady-state photoirradiation of the CT ion pairs indicates that 1-aryl-2-phenoxyethanones are formed as primary photoproducts by oxidation of ketyl radicals by MV^{2+} (under argon) or by molecular oxygen. Small amounts of acetophenones are formed by further photolysis of 1-aryl-2-phenoxyethanones and not by β-fragmentation of the ketyl radicals. The high reactivity of ketyl radicals with oxygen coupled with the low rates of β-fragmentation of the same species have an important bearing in the context of the photoyellowing of lignin containing pulps and papers.

Introduction

When exposed to light, lignin containing pulps and papers undergo color reversion (photoyellowing) that is mainly due to the interaction of lignin functional groups with the UV portion of sunlight.[1] Photoyellowing has an industrial and environmental relevance and in the last

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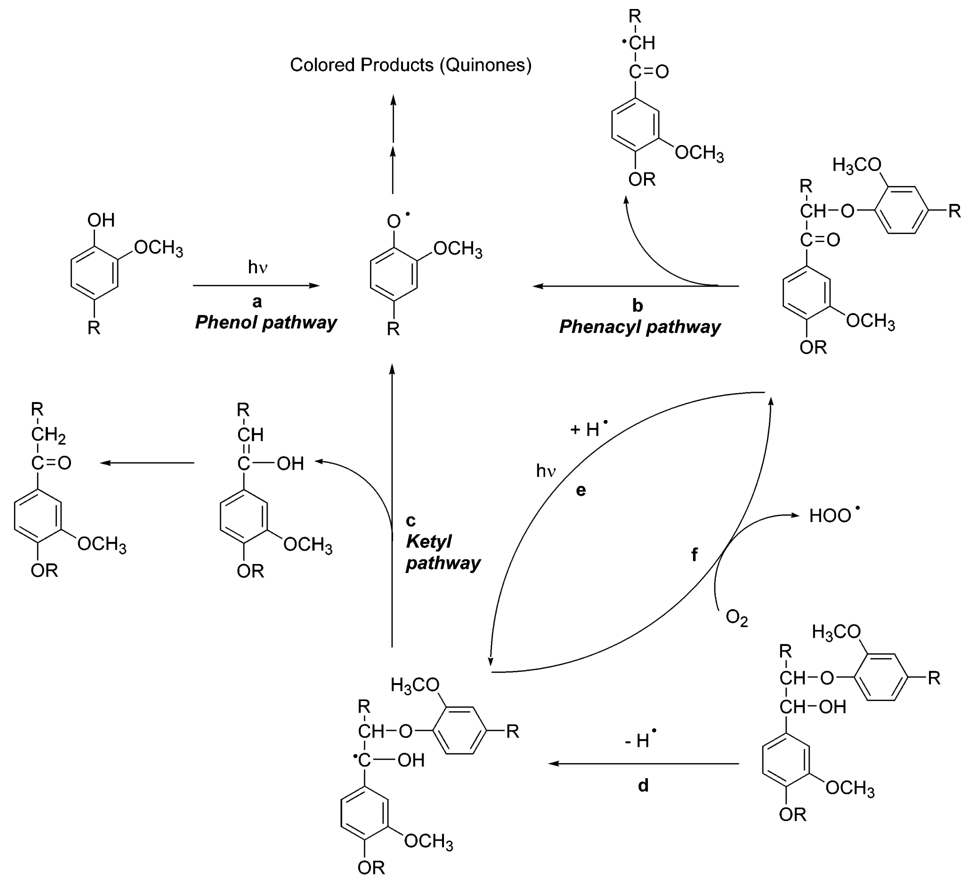
10.1021/jo047826u CCC: $30.25

SCHEME 1



twenty years a considerable effort has been made to understand the mechanistic aspects of this process.[1–4] Such a knowledge is of fundamental importance for the prevention or reduction of photoyellowing by means of chemical modification of functional groups, use of additives such as antioxidants, reducing agents, or UV screens.[2,5–14] Three main reaction pathways have been identified for the photoyellowing process: (1) formation of phenoxyl radicals by direct excitation or hydrogen atom transfer reactions of phenolic groups and further oxidation of phenoxyl radicals to colored products (*phenol pathway*, Scheme 1, path a);[2,15–18] (2) β-cleavage of α-aryloxy substituted aromatic ketones to give a pair of phenoxyl and phenacyl radicals which are precursors of colored products (*phenacyl pathway*, Scheme 1, path b);[2,19–25] and (3) β-cleavage of ketyl radicals (Scheme 1, path c) formed either by photoreduction of aromatic ketones (path e) or by hydrogen abstraction from arylglycerol β-aryl ethers (path d) with formation of phenoxyl radicals and enols which tautomerize to give aromatic ketones (*ketyl pathway*).[2,24,26–28]

The importance of the *ketyl pathway* is due to the great abundance of arylglycerol β-aryl ether structures in lignin (accounting for more than 30% of the phenylpropane units).[29] Several studies have been carried out to assess

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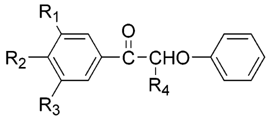
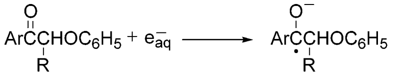
the role of the ketyl pathway in the light-induced yellowing of lignin containing pulps and papers.[24,26,27,30] In this context it is of fundamental importance to determine the rate of fragmentation of ketyl radicals since the ketyl pathway would play a significant role only if the fragmentation process is relatively fast. On the other side, if the lifetime of the ketyl radical is long enough then alternative pathways become available to compete with the β-fragmentation[31] such as reaction with molecular oxygen leading to α-carbonyl-β-aryl ether structures (Scheme 1, path f). In such a case the result would be an increase of the contribution of the *phenacyl pathway* to photoyellowing.[32] In an early study, the ketyl radical generated by hydrogen atom transfer from 1-phenyl-2-phenoxyethanol to the *tert*-butoxyl radical was found to fragment with a relatively high rate constant ($k > 2 \times 10^6$ s^{-1}).[26] An even higher limit ($>5 \times 10^7$ s^{-1}) was given for the rate of fragmentation of the ketyl radical of α-(*p*-methoxyphenoxy)-*p*-methoxyacetophenone.[24] Moreover, product studies of the reaction of *tert*-butoxyl radical with 1-phenyl-2-phenoxyethanol revealed the presence of the products of photofragmentation: phenol and acetophenone.[26] Later on, in a related study, the involvement of the ketyl pathway in the photoyellowing process has been questioned since it was observed that α-phenoxyacetophenone was the primary photoproduct formed by reaction of the ketyl radical of 1-phenyl-2-phenoxyethanol with oxygen (Scheme 1, path f), acetophenone and phenol being formed as secondary photoproducts, and a much lower rate constant, around 10 s^{-1}, was estimated for the fragmentation of 1-phenyl-2-phenoxyethanol-1-yl radical.[30] The relatively long lifetime of this radical was confirmed by kinetic studies, using hydrogen atom abstraction from thiophenol and Arrhenius expression for the β-scission.[33]

However, if the ketyl radicals are characterized by low fragmentation rates it is quite surprising that these species have not been detected and characterized, so far, by using time-resolved techniques. We felt that further studies were needed on this important topic and to this purpose we carried out both time-resolved and product studies by generating ketyl radicals with lignin related structures by means of radiation chemical and photochemical techniques.

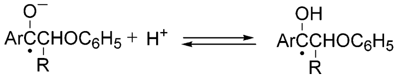
In the radiation chemical studies ketyl radicals have been generated by reaction of α-carbonyl-β-aryl ether lignin models **1**−**7**, which differ in the number and/or position of methoxy substituents, and the presence or absence of a γ methyl group, with the solvated electron produced by pulse radiolysis of an aqueous solution (eq 1) as reported by Scaiano for the generation of the ketyl radical of α-(*p*-methoxyphenoxy)-*p*-methoxyacetophenone.[24] The radical anion thus produced by reduction of the ketone in neutral or acidic conditions can be rapidly protonated by the solvent to form the ketyl radical (eq 2).



1 $R_1, R_2, R_3, R_4 = H$
2 $R_1, R_3, R_4 = H, R_2 = OCH_3$
3 $R_3, R_4 = H, R_1, R_2 = OCH_3$
4 $R_4 = H, R_1, R_2, R_3 = OCH_3$
5 $R_1, R_2, R_3 = H, R_4 = CH_3$
6 $R_1, R_3 = H, R_2 = OCH_3, R_4 = CH_3$
7 $R_3 = H, R_1, R_2 = OCH_3, R_4 = CH_3$

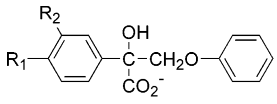


$$\mathrm{Ar\overset{O}{\overset{\|}{C}}\underset{R}{CH}OC_6H_5} + e^-_{aq} \longrightarrow \mathrm{Ar\overset{O^-}{\underset{\bullet}{C}}\underset{R}{CH}OC_6H_5} \qquad (1)$$



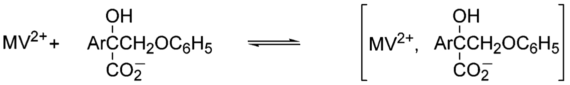
$$\mathrm{Ar\overset{O^-}{\underset{\bullet}{C}}\underset{R}{CH}OC_6H_5} + H^+ \rightleftharpoons \mathrm{Ar\overset{OH}{\underset{\bullet}{C}}\underset{R}{CH}OC_6H_5} \qquad (2)$$

In the photochemical studies, ketyl radicals have been produced by charge-transfer photoactivation of the electron donor−acceptor salts of methyl viologen (MV^{2+}) with carboxylate donors, α-hydroxy-α-phenoxymethyl-aryl acetates **8**−**10**.[34] Photoexcitation of these CT complexes

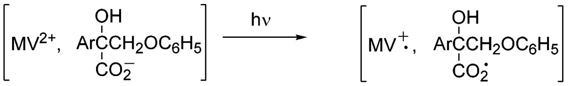


8 $R_1, R_2 = H$
9 $R_1 = OCH_3, R_2 = H$
10 $R_1, R_2 = OCH_3$

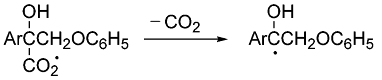
leads to the instantaneous formation of the reduced acceptor (methyl viologen radical cation, $MV^{+\bullet}$) and an acyloxyl radical [$ArC(CO_2^\bullet)(OH)CH_2(OC_6H_5)$] (eq 4), which undergoes a fast decarboxylation[35,36] with formation of a ketyl radical (eq 5). Both time-resolved spectroscopic (laser flash photolysis) and product studies (steady-state irradiation) have been carried out.



$$MV^{2+} + \mathrm{Ar\overset{OH}{C}\underset{CO_2^-}{}CH_2OC_6H_5} \rightleftharpoons \left[MV^{2+},\ \mathrm{Ar\overset{OH}{C}\underset{CO_2^-}{}CH_2OC_6H_5}\right] \qquad (3)$$



$$\left[MV^{2+},\ \mathrm{Ar\overset{OH}{C}\underset{CO_2^-}{}CH_2OC_6H_5}\right] \xrightarrow{h\nu} \left[MV^{+\bullet},\ \mathrm{Ar\overset{OH}{C}\underset{CO_2^\bullet}{}CH_2OC_6H_5}\right] \qquad (4)$$



$$\mathrm{Ar\overset{OH}{C}\underset{CO_2^\bullet}{}CH_2OC_6H_5} \xrightarrow{-CO_2} \mathrm{Ar\overset{OH}{\underset{\bullet}{C}}CH_2OC_6H_5} \qquad (5)$$

Results

Pulse Radiolysis Study. Ketyl radicals were generated in aqueous solution containing 2-methyl-2-propanol

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TABLE 1. Spectral Data for the Ketyl Radicals and Radical Anions Generated by Pulse Radiolysis of Aqueous Solutions at pH ~6.0 and ~11.0 Containing the Ketones 1−7

	pH 6.0		pH 11.0	
ketone	λ_{max}/nm	ϵ_{max}/M^{-1} cm^{-1}	λ_{max}/nm	ϵ_{max}/M^{-1} cm^{-1}
1	380, 440	1000, 600	330, 390, 460	1700, 700, 800
2	330, 430, 560	2700, 700, 1200	330, 540	2800, 1300
3	340, 490, 590	2400, 900, 1000	340, 600	2900, 1200
4	350, 450, 560	1600, 1400, 700	350, 460, 540	2000, 1200, 1000
5	330, 370, 450	1700, 1000, 700	330, 460	3000, 900
6	330, 430, 540	3900, 800, 1300	340, 520	4700, 1500
7	340, 490, 580	3800, 1200, 1200	340, 580	4400, 1400

(1 M) by reaction of α-carbonyl-*β*-aryl ether lignin models **1**−**7** with the solvated electrons (eqs 1 and 2). The hydrated electron (e_{aq}^-) reacts with the ketone leading to the ketyl radical anion (eq 1), with diffusion controlled rates.[37] 2-Methyl-2-propanol was added to scavenge the hydroxyl radical •OH (eq 7, $k = 6 \times 10^8$ M^{-1}s^{-1})[38] and to increase the solubility of the ketone. Experiments were carried out in neutral (pH 6.0) and basic (pH 11.0) conditions under argon, air or N_2/O_2 9:1 (v/v). As an example, in Figure 1 are displayed the time-resolved absorption spectra observed on reaction of e_{aq}^- with **2** in argon saturated aqueous solutions at pH 6.0 and 11.0, recorded 20 *μ*s after the electron pulse.

$$H_2O \rightsquigarrow H^+, {}^{\bullet}OH, e^-_{aq} \qquad (6)$$

$$^{\bullet}OH + CH_3C(CH_3)_2OH \longrightarrow H_2O + \dot{C}H_2C(CH_3)_2OH \qquad (7)$$

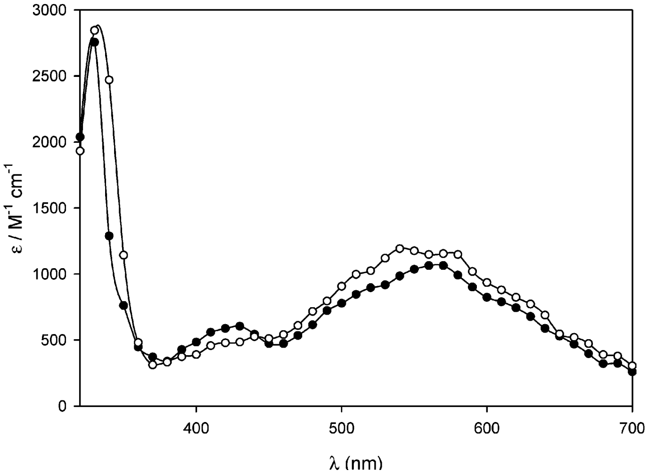

FIGURE 1. Time-resolved absorption spectra observed on reaction of e_{aq}^- with **2** (0.2 mM) at $T = 25$ °C, recorded after pulse radiolysis of an Ar-saturated aqueous solution at pH 6.0 (filled circles) and at pH 11 (empty circles), containing 1 M 2-methyl-2-propanol at 20 *μ*s after the 1 *μ*s, 10-MeV electron pulse.

At pH 6.0 (filled circles) the spectrum shows three absorption bands centered around 330, 430, and 560 nm. This spectrum can be reasonably assigned to the ketyl radical **2H•** and is comparable with the spectrum of the ketyl radical, produced in the same way by pulse radiolysis of 4-methoxyacetophenone, which displayed three absorption bands centered at 310, 410, and 520 nm.[39] The three absorption bands are all quenched by oxygen, with the same rate, as expected for a carbon centered radical. An analogous behavior was observed with substrates **1**, **3**−**7.** The spectral data of the ketyl radicals are reported in Table 1. The UV−vis spectra of ketyl radicals **1H•**, **3H•**, and **5H•**−**7H•** are reported in the Supporting Information. The comparison of the absorption spectra of **1H•** and **5H•**, **2H•** and **6H•**, and **3H•** and **7H•** shows that the presence of the *γ*-methyl group has no significant effect on the position and relative intensities of the absorption bands. The comparison of the absorption spectra of **1H•**, **2H•**, **3H•**, and **4H•**, and of **5H•**, **6H•**, and **7H•** shows instead that the nature of the ring substituent has a significant effect on the position and relative intensities of the absorption bands.

When the spectrum was recorded in alkaline solution (see Figure 1, open circles), the shape and position of the absorption bands slightly changed. The bands should now be assigned to $\mathbf{2}^{-\bullet}$ on the basis of a p$K_a \approx 9-10$ that can be estimated for the acid−base equilibrium between **2H•** and $\mathbf{2}^{-\bullet}$ (eq 2). An accurate determination of the pK_a value for **2H•**, by measuring the absorption at a suitable wavelength as a function of pH, was not possible due to the small difference in the absorption between the ketyl radical and the ketyl radical anion. A pK_a value of 9.5 was instead determined for **4H•**, and in this case the difference in the absorption between **4H•** and $\mathbf{4}^{-\bullet}$ at 450 nm is sufficiently large. The UV−vis spectra of **4H•** and $\mathbf{4}^{-\bullet}$ are reported in Figure 2. In the inset, the plot of ΔOD, monitored at 450 nm vs pH is also shown.

The spectral data for $\mathbf{1}^{-\bullet}$−$\mathbf{7}^{-\bullet}$ are collected in Table 1. The UV−vis spectra of $\mathbf{1}^{-\bullet}$, $\mathbf{3}^{-\bullet}$, and $\mathbf{5}^{-\bullet}$−$\mathbf{7}^{-\bullet}$ are reported in the Supporting Information.

In neutral solution, the rate of decay of **1H•**−**7H•** was measured spectrophotometrically by following the change in optical density at the wavelengths corresponding to the UV and visible absorption maxima (see Table 1). Under these conditions the ketyl radicals were found to decay by a second-order reaction and the same value of the decay rate was determined for all the absorption bands, fully supporting their assignment to the same

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(35) This process is too fast ($k > 10^7$ s^{-1}) to be followed in the nanosecond time scale.[34,36]

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(39) The absorption spectrum of the ketyl radical 4-MeOC$_6$H$_4$C•(OH)-CH$_3$ was recorded 20 *μ*s after pulse radiolysis (3 MeV van de Graaf accelerator, 300 ns electron pulse, 5 Gy/pulse) of an argon saturated aqueous solution (pH 5.5) containing 4-methoxyacetophenone (0.05 mM) and 2-methyl-2-propanol (0.1 M).

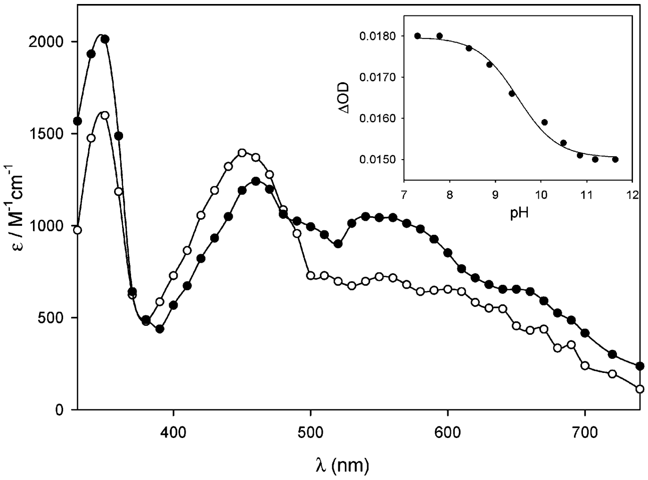


FIGURE 2. Time-resolved absorption spectra observed on reaction of e_{aq}^- with **4** (0.2 mM) at $T = 25$ °C, recorded after pulse radiolysis of an Ar-saturated aqueous solution at pH 6 (empty circles) and at pH 11 (filled circles), containing 1 M 2-methyl-2-propanol at 20 μs after the 1 μs, 10-MeV electron pulse. Inset: Plot of ΔOD monitored at 450 nm vs pH. From the curve fit pK_a = 9.5.

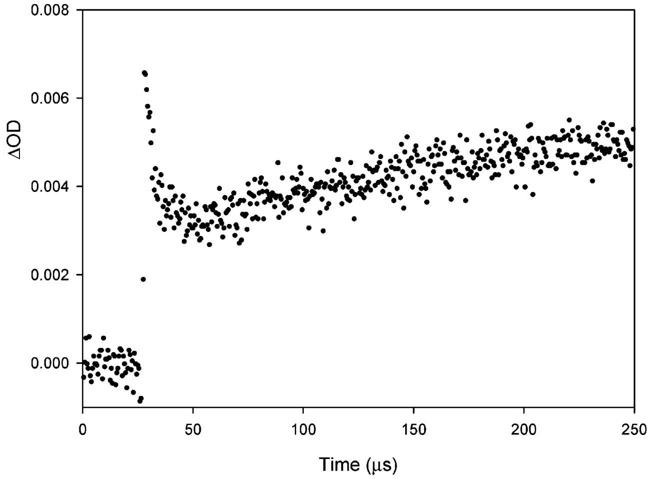
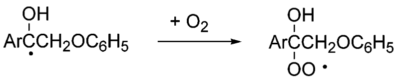


FIGURE 3. Decay and following buildup of the absorption at 350 nm observed after pulse radiolysis of an aqueous solution of **3** (0.2 mM) at $T = 25$ °C, saturated with a 9:1 N_2/O_2 mixture at pH 6.0, containing 1 M 2-methyl-2-propanol after the 1 μs, 10-MeV electron pulse.

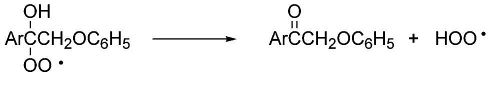
transient species. The rate of decay was found to be highly dose-dependent and at the lowest doses that allowed a reliable measurement of the decay rates (ca. 3.5 Gy/pulse), the decays better fitted first-order kinetics. The rate constants for the decay of **1H**$^\bullet$−**7H**$^\bullet$ determined at low doses under argon were very similar and comprised in the range (1.7−2.7) × 10^3 s^{-1}.

When the solutions were air saturated a very fast decay of the ketyl radical bands was observed. Under these conditions it was not possible to measure the rate of reaction of ketyl radicals with molecular oxygen. To this purpose the solutions were saturated with O_2 (10% (v/v) in N_2). The rate of the reaction of **1H**$^\bullet$−**7H**$^\bullet$ with oxygen was measured spectrophotometrically by following the change in optical density at the wavelengths corresponding to the UV and visible absorption maxima reported in Table 1. The second-order rate constants have been calculated by dividing the pseudo-first-order rate constants k_{obs} for the concentration of oxygen (0.15 mM).[40] The rates of reaction of **1H**$^\bullet$−**7H**$^\bullet$ with molecular oxygen are very similar and lie in the range (1.8−2.7) × 10^9 $M^{-1}s^{-1}$.

The decay of the ketyl radicals **3H**$^\bullet$, **4H**$^\bullet$, and **7H**$^\bullet$ is accompanied by the formation of stable products, likely the starting ketones, which absorb around 350 nm. In Figure 3 it can be noticed that the buildup of the ketone **3** is slower than the decay of **3H**$^\bullet$ and is somewhat delayed. This is due to the fact that the reaction of the ketyl radicals with O_2 leads to the formation of α-hydroxyperoxyl radicals (eq 8) from which the ketones are formed by release of hydroperoxyl radical HOO$^\bullet$ (eq 9).[41]



$$\mathrm{Ar\overset{OH}{\underset{\bullet}{C}}CH_2OC_6H_5} \xrightarrow{+\,O_2} \mathrm{Ar\overset{OH}{\underset{OO\,\bullet}{C}}CH_2OC_6H_5} \qquad (8)$$



$$\mathrm{Ar\overset{OH}{\underset{OO\,\bullet}{C}}CH_2OC_6H_5} \longrightarrow \mathrm{Ar\overset{O}{\overset{\|}{C}}CH_2OC_6H_5} + \mathrm{HOO^\bullet} \qquad (9)$$

Steady-State Photoirradiation. Aqueous solutions of methyl viologen triflate [$MV(OTf)_2$] and of the sodium salt of the carboxylate anions **8**−**10** (generated in situ by dissolution of the free carboxylic acid in aqueous sodium bicarbonate) were saturated with argon or oxygen and then irradiated for 1 h in a photoreactor equipped with 10 × 14 W black phosphorus lamps with emission at λ_{MAX} 360 nm. A deep blue coloration of the solution characteristic of $MV^{+\bullet}$ developed in the steady-state photoirradiation under argon.[42] After extraction with chloroform, reaction products were analyzed by ^{1}H NMR. The results are reported in Table 2. The mass balance was always satisfactory, accounting for more than 85% of the starting material.

The photoirradiation of the [MV^{2+}/**8**] ion pair, under argon, leads to the formation of 1-phenyl-2-phenoxy ethanone (**1**) as the major photoproduct. Acetophenone was formed in very small amounts (<1% referred to the starting material). Higher yields of **1** were observed when the solution was saturated with oxygen. Similar results were also obtained in the photoirradiation of the [MV^{2+}/**9**] ion pair. The major product, 1-(4-methoxyphenyl)-2-phenoxy ethanone (**2**), is accompanied by small amounts of 4-methoxyacetophenone, 2-(2-hydroxyphenyl)-4-methoxyacetophenone, and 2-(4-hydroxyphenyl)-4-methoxyacetophenone. Also in this case a significant increase of the reaction yields was observed under oxygen. When the reaction time was reduced to 15 min, only traces of 4-methoxyacetophenone were observed. Photoirradiation of the [MV^{2+}/**10**] ion pair again led to 1-(3,4-dimethoxyphenyl)-2-phenoxy ethanone (**3**) as the major photoproduct accompanied by minor amounts of 2-(2-hydroxyphenyl)-3,4-dimethoxyacetophenone and 2-(4-hydroxyphenyl)-3,4-dimethoxyacetophenone and of 3,4-dimethoxyacetophenone. As in the photoirradiation of the [MV^{2+}/**9**] ion pair, higher yields of products were observed

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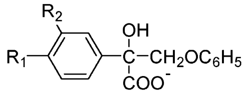
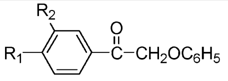
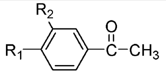
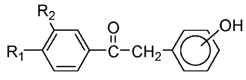
[40] Murov, S. L.; Carmicael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

[41] *The Chemistry of Free Radicals*: *Peroxyl Radicals*. Alfassi, Z. V., Ed.; John Wiley & Sons: New York, 1997. von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor & Francis: London, UK, 1987.

[42] Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617. Bockman, T. M.; Kochi, J. K. *J. Org. Chem.* **1990**, *55*, 4127.

TABLE 2. Products and Yields in the Photoirradiation of MV^{2+}/8−10 Ion Pairs

Substrates		Reaction Products		
				
8 (R_1, R_2 = H)	Ar 60 min	15	<1	
	O_2 60 min	25	<1	
	O_2 15 min	12	-	
9 (R_1 = OCH_3, R_2 = H)	Ar 60 min	20	1	1
	O_2 60 min	52	4	2
	O_2 15 min	24	<1	<1
10 (R_1, R_2 = OCH_3)	Ar 60 min	11	2	7
	O_2 60 min	22	3	19
	O_2 15 min	10	1	4

[a] Yields are referred to the initial amount of the substrate. Average of three determinations, error ±5%.

when the solution was saturated with oxygen moreover the relative amounts of minor photoproducts was reduced by decreasing the irradiation time to 15 min. In a control experiment it was observed that photoirradiation of 1-(3,4-dimethoxyphenyl)-2-phenoxy ethanone (**3**) in H_2O/CH_3CN 3:2, under the same experimental conditions used for the irradiation of the [MV^{2+}/**10**] ion pair, led to the formation of 3,4-dimethoxyacetophenone, 2-(2-hydroxyphenyl)-3,4-dimethoxyacetophenone, and 2-(4-hydroxyphenyl)-3,4-dimethoxyacetophenone.

Laser Flash Photolysis Study. Time-resolved laser flash photolysis studies have been carried out only with the carboxylate **9**, which gave the higher yields of photoproducts. In Figure 4 is shown the transient spectrum (filled circles) observed 200 ns after 355 nm laser flash photolysis of an argon saturated aqueous solution of $MV(OTf)_2$ (20 mM) and **9** (20 mM). The spectrum showed two bands: a strong, sharp band with $\lambda_{MAX} = 390$ nm and a broad absorption band in the visible region that can be assigned to the reduced form of methyl viologen ($MV^{+\bullet}$), the absorption spectrum of which has two maxima (390 and 605 nm) in aqueous solution.[42] Analysis of the spectral evolution in the former 2 μs indicates that the bands at 390 and 600 nm increase slightly in intensity (Figure 4, insets a and c), while, on the same time scale, the absorption in the 400−550 nm region decreases in intensity (Figure 4, inset b). It is likely that the latter absorption is due to the presence of the ketyl radical **2H$^\bullet$**, which is formed according to eq 5. The absorption band of this species is not distinguishable in the spectrum reported in Figure 4 due to its weak absorption, which is significantly smaller than that of $MV^{+\bullet}$.[42]

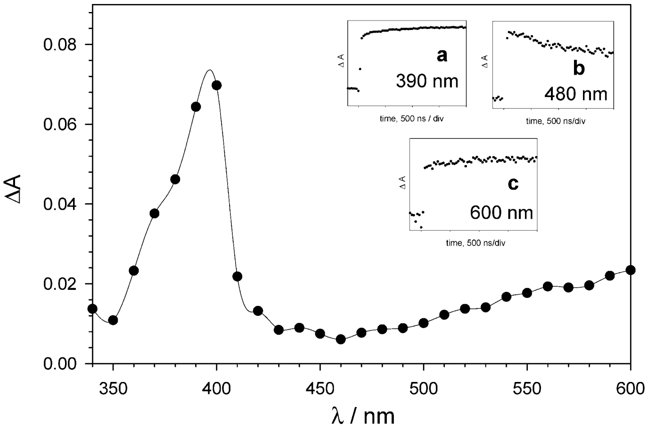
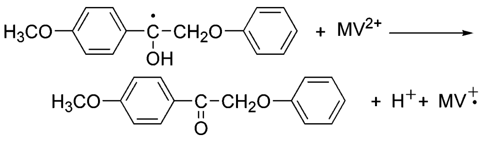


FIGURE 4. Time-resolved absorption spectra recorded 200 ns (filled circles) following the 8-ns laser excitation (355 nm) of an Ar-saturated aqueous solution of the [MV^{2+}/**9**] ion pair. Insets: (a) Buildup of the absorption at 390 nm. (b) Decay of the absorption at 480 nm. (c) Buildup of the absorption at 600 nm.

The decrease in absorbance in the 400−550 nm region and the increase in absorbance at 390 and 600 nm are likely due to the relatively fast oxidation of **2H$^\bullet$** by MV^{2+} (eq 10), which produces an additional amount of $MV^{+\bullet}$.[34,43] **2H$^\bullet$** should be characterized by a very low oxidation potential[44] and can be easily oxidized by MV^{2+}.[42]



(10)

Discussion

Reaction of α-carbonyl-β-aryl ether lignin models **1**−**7** with the solvated electrons produced by pulse radiolysis

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[43] Barnett, J. R.; Hopkins, A. S.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 80.

[44] An $E_{1/2}$ value of −0.46 V vs SCE in CH_3CN was obtained by photomodulated voltammetry for the ketyl radical 4-$CH_3C_6H_4C^\bullet(OH)$-CH_3.[45]

of aqueous solutions allowed the spectral characterization of ketyl radicals **1H**$^•$−**7H**$^•$. The assignment of the absorption spectra observed after the pulse to the ketyl radicals is supported by the fact that a similar spectrum is produced in the same way by pulse radiolysis of 4-methoxyacetophenone. Moreover, in accordance with the assignment of the absorption bands to a carbon centered radical, they are all quenched by oxygen. Finally, when the spectra were recorded in alkaline solution, the shape and position of the absorption bands slightly changed being now assigned to the ketyl radical anions. By measuring the absorption at 450 nm as a function of pH, the pK_a for the acid−base equilibrium between **4H**$^•$ and **4**$^{-•}$ has been determined. The value obtained (9.5) is typical for α-hydroxyalkyl radicals of related structures.[45,46]

It is interesting to note that our observation of the transient absorption spectra of ketyl radicals **1H**$^•$−**7H**$^•$ is in contrast with the results of Scaiano and co-workers, who were unable to observe the ketyl radical of α-(*p*-methoxyphenoxy)-*p*-methoxyacetophenone.[24] The only transient observed after the pulse was the 4-methoxyphenoxyl radical and this result was interpreted with a *β*-fragmentation process of the ketyl radical too fast to be followed spectrophotometrically ($k > 5 \times 10^7$ s^{-1}). The rate of decay of the ketyl radicals **1H**$^•$−**7H**$^•$, measured spectrophotometrically by us under acidic conditions, following the change in optical density at the wavelengths corresponding to the UV and visible absorption maxima (330−380 nm, 430−490 nm, and 540−590 nm), are indeed more than 4 orders of magnitude lower than 5×10^7 s^{-1}. Ketyl radicals were found to decay by a second-order reaction and the rate of decay was found to be highly dose dependent. At lowest doses that allowed a reliable determination of the rate constants (ca. 3.5 Gy/pulse) the decay rates for the ketyl radicals **1H**$^•$−**7H**$^•$ were found to obey a first-order process. The values are very similar and comprised in the range 1.7×10^3 to 2.7×10^3 s^{-1}, thus the decay of the ketyl radicals does not change significantly by increasing the number of aryl methoxy substituents or in the presence of a *γ*-methyl substituent.[47] Since the rate of decay of the ketyl radicals measured by us should be considered an upper limit for the rate of *β*-fragmentation, our results are more in accordance with the low fragmentation rate determined by Mulder and co-workers for the fragmentation of 1-phenyl-2-phenoxyethanol-1-yl radical.[30]

Analysis of the time-resolved absorption spectra of **3H**$^•$, **4H**$^•$, and **7H**$^•$ under oxygen showed that the decay of the ketyl radicals is accompanied by the formation of stable products, i.e., the starting ketones **3**, **4**, and **7**. It was also observed that the buildup of the ketones was slower than the decay of the ketyl radicals and somewhat delayed. Thus, in this time scale, it was possible to follow the reaction of the ketyl radicals **3H**$^•$, **4H**$^•$, and **7H**$^•$ with O_2 leading to the formation of the α-hydroxyperoxyl radicals (eq 8) and the subsequent formation of ketones **3**, **4**, and **7** by release of hydroperoxyl radicals HOO$^•$ (eq 9).[41] The second-order rate constants for the reaction of ketyl radicals with molecular oxygen are typical for reactions of carbon-centered radicals with oxygen[48] and are very close together. Determination of the rate of reaction of ketyl radicals with molecular oxygen (eq 8) is an important result of this study, which has a bearing in the context of the photoyellowing process. The high reactivity of ketyl radicals with lignin-related structures **1H**$^•$−**7H**$^•$ with oxygen coupled with the low rates of *β*-fragmentation of the same species suggests that α-aryloxy substituted aromatic ketones should be formed preferentially with respect to the products of fragmentation (aromatic ketones and phenoxyl radicals). This hypothesis is fully supported by the results of the steady-state photoirradiation (vide infra).

The results of the steady-state photoirradiation and laser flash photolysis experiments can be rationalized on the basis of reactions 3−5 and 10. Photoexcitation of the CT ion pairs [MV^{2+}/**8**−**10**] leads to the instantaneous formation of the reduced acceptor (methyl viologen radical cation, MV$^{+•}$) and an acyloxyl radical [ArC(CO$_2^•$)(OH)-CH$_2$(OC$_6$H$_5$)] (eq 4), which undergoes a very fast decarboxylation with formation of ketyl radicals (eq 5).[34] The formation of MV$^{+•}$ is clearly visible by the deep blue coloration that developed in the steady-state photoirradiation under argon and, in the LFP experiment with the [MV^{2+}/**9**] ion pair, by the observation of the two absorption bands of MV$^{+•}$ centered at 390 and 605 nm.[42] The absorption of the ketyl radical **2H**$^•$ is not distinguishable in the spectrum due to its relative low absorption as compared to that of MV$^{+•}$. Analysis of the spectral evolution in the former 2 μs indicates that an additional small amount of MV$^{+•}$ is formed after the laser pulse by oxidation of the ketyl radical **2H**$^•$ induced by MV^{2+} (eq 10). The occurrence of reaction 10 is also supported by the formation of 1-(4-methoxyphenyl)-2-phenoxyethanone, the product of oxidation of **2H**$^•$, in the steady-state photoirradiation of the CT ion pair [MV^{2+}/**9**].

The analysis of the results of steady-state photoirradiation of the CT ion pairs [MV^{2+}/**8**−**10**] clearly indicates that 1-aryl-2-phenoxyethanones **1**−**3** are formed as primary photoproducts. The small amounts of acetophenones are likely formed by further photolysis of 1-aryl-2-phenoxyethanones and not by *β*-fragmentation of the ketyl radicals. Accordingly, under oxygen atmosphere, it was observed that the yields of acetophenones relative to those of 1-aryl-2-phenoxyethanones decreased significantly by reducing the irradiation time from 60 to 15 min. This hypothesis is confirmed by the observation of the α-carbonyl *β*-1 products, 2-(2-hydroxyphenyl)-4-methoxyacetophenone and 2-(4-hydroxyphenyl)-4-methoxyacetophenone, in the steady-state irradiation of the [MV^{2+}/**9**] ion pair and 2-(2-hydroxyphenyl)-3,4-dimethoxyacetophenone and 2-(4-hydroxyphenyl)-3,4-dimethoxyacetophenone in the steady-state irradiation of the [MV^{2+}/**10**] ion pair. These products are formed according to the mechanistic pathways already described in the photoirradiation of 3,4-dimethoxy-α-(2′-methoxyphenoxy)acetophenone (guaiacylacetoveratrone) in ethanol/water

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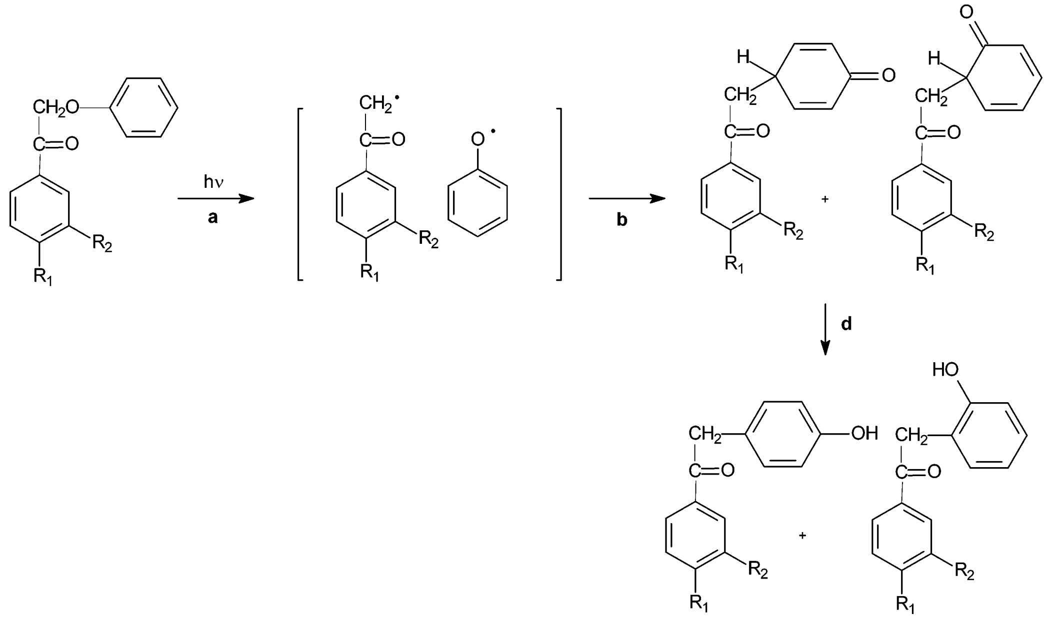
[45] Lund, T.; Wayner, D. D. M.; Jonsson, M.; Larsen, A. G.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, *123*, 12590−12595.

[46] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley: New York, 1980.

[47] While substituent effects on the phenyl ring α to the radical center should not significantly affect the rate of scission of the ketyl radical, a substitution to the 2-position may enhance the rate of *β*-scission.[33]

[48] Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095−5099.

SCHEME 2



mixture.[49] When excited, 1-aryl-2-phenoxyethanones undergo an intramolecular β-cleavage leading to a phenoxyl and phenacyl radical pair. In cage recombination of the radical pair leads to a cyclohexadienone coupling product that, via a prototropic rearrangement, is converted into the α-carbonyl β-1 compounds (Scheme 2).[4,19,20,51]

The amount of secondary photoproducts increases by increasing the number of aryl methoxy substituents, in the order **8** < **9** < **10**, in accordance with the fact that the absorption of light emitted from the lamps by products 1-aryl-2-phenoxyethanones increases in the order **1** < **2** < **3**.

Significantly higher yields of photoproducts were observed when the solutions of the [MV^{2+}/**8**−**10**] ion pairs were saturated with oxygen. In argon degassed solutions, photogenerated $MV^{+\bullet}$ absorbs the light emitted by the lamps and an "inner filter" effect results which prevents efficient photolysis.[34] In the presence of oxygen, $MV^{+\bullet}$ does not accumulate since it is rapidly oxidized to MV^{2+} (eq 11) and the solutions does not develop the characteristic blue coloration of the reduced viologen.[52]

$$MV^{+\bullet} + O_2 \rightarrow MV^{2+} + O_2^{-\bullet} \tag{11}$$

Since no fragmentation products have been observed as primary photoproducts in the steady-state irradiation either under argon or in the presence of oxygen, it derives that β-fragmentation of the ketyl radicals **1H**$^\bullet$−**3H**$^\bullet$ is significantly slower than their oxidation induced by MV^{2+} (eq 10) or by molecular oxygen (eq 8).

Conclusions

Detection and spectral characterization of ketyl radicals with lignin related structures was accomplished for the first time by using time-resolved techniques. By combining all the information thus obtained with the different precursors and methods of generation of the ketyl radicals, we gave a better insight into some of the unsolved mechanistic aspects associated with the photoyellowing of lignin containing pulps and papers. Low fragmentation rates of ketyl radicals appear to be a rather general process. The implication for the lignin photochemistry is that a ketyl radical of this type will not cleave to produce aromatic ketones and phenoxyl radicals fast and efficiently so that there is the possibility of scavenging them, i.e., by reaction with molecular oxygen, before the cleavage occurs. Thus, only a minor role is played by the ketyl pathway in the photoyellowing process. A major role would instead be played by the β-cleavage of α-aryloxy-substituted aromatic ketones (*phenacyl pathway*) that are formed by the reaction of ketyl radicals with O_2.

Experimental Section

Materials. All the reagents and solvents were of the highest commercial quality available and were used without further purification (unless otherwise specified). Milli-Q-filtered water was used for all solutions. Methyl viologen ditriflate was prepared according to a procedure reported in the literature.[34]

Pulse Radiolysis Experiments. The pulse radiolysis experiments were performed using a 10 MeV electron linear accelerator, which supplied 0.2−2 μs pulses with doses between 2 and 20 Gy. Dosimetry was performed with N_2O-saturated 10^{-2} M aqueous KSCN solutions, for which $G[(SCN)_2^{-\bullet}] = 6.0 \times 10^{-7}$ mol J^{-1} and $\epsilon[(SCN)_2^{-\bullet}] = 7600$ M^{-1} cm^{-1} at 480 nm.[53] Experiments were performed at room temperature, using aqueous solutions containing the substrate (0.2 mM) and 2-methyl-2-propanol (1 M). Solutions were saturated with argon, oxygen, or a 9:1 N_2/O_2 mixture. Experiments were performed at pH 6 (5 mM Na_2HPO_4 adjusted with 0.1 M $HClO_4$) and at pH 11 (5 mM $Na_2B_4O_7{\cdot}10H_2O$ adjusted with 0.1 M NaOH). A flow system was employed in all the experiments. The rate constants were obtained by averaging

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[49] In polar solvents β-cleavage should occur from both singlet and triplet states.[22,50]

[50] Wan, J. K. S.; Tse, M. Y.; Depew, M. C. *Res. Chem. Intermed.* **1992**, *17*, 59−75.

[51] Castellan, A.; Zhu, J. H.; Colombo, N.; Nourmamode, A.; Davidson, R. S.; Dunn, L. *J. Photochem. Photobiol. A* **1991**, *58*, 263−273.

[52] Rodgers, M. A. J. *Radiat. Phys. Chem.* **1984**, *23*, 245. Tsukuhara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632.

[53] Schuler, R. H.; Hartzell, A. L.; Behar, B. *J. Phys. Chem.* **1981**, *85*, 192.

3 to 5 values, each consisting of the average of 3 to 10 shots, and were reproducible to within 5%.

The pK_a value for the acid−base equilibria between the ketyl radical **4H$^•$** and the ketyl radical anion **4$^{-•}$** was determined by plotting ΔA as a function of pH at 450 nm (where the difference in absorption between radical cation and radical zwitterion is sufficiently large) in the pH range 7−12. The ΔA vs pH curve was fitted to the following equation: $\Delta A = [\Delta A_0 + \Delta A_1 \times 10^{(\mathrm{pH}-\mathrm{p}Ka)}]/1 + 10^{(\mathrm{pH}-\mathrm{p}Ka)}$.

Preparation of Samples for Steady-State Photooxidation and Laser Flash Photolysis. Aqueous solutions of the sodium salt of the α-hydroxycarboxylates of substrates **8**−**10** were prepared by addying 50, 20, or 10 μmol of the free acid and 55, 22, or 11 μmol of $NaHCO_3$, respectively, to 1 mL of Milli-Q-filtered water. Different concentrations of the three substrates were chosen in order to have an absorbance of the charge-transfer complexes at 350 nm of ca. 1. The solutions were sonicated until complete dissolution then filtered and transferred to a Pyrex test tube. An equimolar amount of methyl viologen ditriflate with respect to the substrate was then added. The solutions were saturated with argon or with oxygen and then photoirradiated for 15 or 60 min. At the end the internal standard (phenylacetic acid) was added. The solutions were acidified, extracted with chloroform, and dried over anhydrous Na_2SO_4 and the solvent was evaporated. The products were analyzed by ^{1}H NMR.

Laser Flash Photolysis Studies. Laser flash photolysis experiments were carried out by irradiating a 3 mL Suprasil quartz cell (10 mm × 10 mm) containing an argon-saturated aqueous solution of the sodium salt of **9** (20 mM), prepared as described in the steady-state photoirradiation, and of methyl viologen ditriflate (20 mM). The experiments were carried out at $T = 25 \pm 0.5$ °C under magnetic stirring.

Acknowledgment. Thanks are due to the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) and the Consiglio Nazionale delle Ricerche (CNR) for financial support. Pulse radiolysis experiments were performed at the Free Radical Research Facility of Daresbury, Cheshire, UK, with the support of the European Commission through the Access to Large-Scale Facilities activity of the TMR Program. The authors also thank Prof. Suppiah Navaratnam and Dr. Ruth Edge for technical assistance.

Supporting Information Available: Instrumentation; syntheses of substrates **1**−**10**. The UV−vis absorption spectra of ketyl radicals **1H$^•$**, **3H$^•$**−**7H$^•$** and UV−vis absorption spectra of ketyl radical anions **1$^{-•}$**, **3$^{-•}$**−**7$^{-•}$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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