Reduced Radical Characteristics of 7-Aminocoumarin Dyes Studied by Pulse Radiolysis Technique

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Received: February 1, 2002; In Final Form: May 4, 2002

Characteristics of the reduced radicals of a series of 7-aminocoumarin dyes (C) have been investigated in different solvents using pulse radiolysis (PR) technique. Since these coumarin dyes are almost insoluble in water, a mixed solvent (MS) system containing 5.0 mol dm^{-3} of 2-propanol (2PNL) and 1.0 mol dm^{-3} of acetone (ACT) in water has been used in the present work to substitute the aqueous solvent. In MS, for a wide pH range of ∼1−9, the reduced coumarin radicals are formed in the neutral form, $CH^•$. These radicals show two absorption bands, one in the 300−400 nm region and the other in the 500−600 nm region. As the coumarin dyes undergo hydrolysis in strongly alkaline solutions, PR studies in MS could not be extended beyond pH ∼9. In 2PNL, the reduced coumarin radicals are also formed in the $CH^•$ form, even in the presence of ∼1 mol dm^{-3} of a strong proton acceptor like triethylamine (TEA). Since the pK_b value of TEA is 3.19, it is indicated that the acid dissociation constant of the $CH^•$ radicals (pK_a^R) must be >11. The PR results in MS and 2PNL clearly indicate that the anionic form of the reduced coumarin radicals ($C^{•-}$) formed by initial one-electron reduction of the dyes undergo very fast protonation to give the $CH^•$ form in the solution. To avoid protonation of $C^{•-}$, PR experiments were carried out in acetonitrile (ACN) solutions in the presence of ∼1 mol dm^{-3} of aniline (AN). With this high concentration, AN efficiently scavenges the cation radicals from the solvent ion pairs ($ACN^{+}\cdots e^{-}$) formed following the electron pulse, and thus the equivalent amount of electrons become available to reduce C to $C^{•-}$. It is seen that the $C^{•-}$ radicals of all the coumarin dyes studied have unusually weak absorption bands in the 500−800 nm region. Since the coumarin dyes are good electron acceptors, present results on $CH^•$ and $C^{•-}$ radicals will be useful in elucidating the ET mechanism using coumarin dyes as the electron acceptors.

1. Introduction

Coumarins, the derivatives of 1,2-benzopyrone, are the well-known laser dyes for the blue-green region.[1−7] Among different coumarin dyes, the ones having amino substituents (NH_2 or NR_2; R being the alkyl or cycloalkyl groups) at the 7-position of the 1,2-benzopyrone moiety have found to be of special significance in relation to their laser activity and many other applications. The fluorescence quantum yields of these molecules are usually very high, often close to unity.[1−9] In most of these dyes, the internal conversion and intersystem crossing processes are found to be almost negligible.[8,9] The 7-aminocoumarin dyes undergo substantial change in their dipole moment on excitation from the ground to the excited S_1 state.[1−9] Thus, these molecules are found to be suitable probes in investigating many physical and physiochemical processes in the condensed phase, making use of their fluorescence properties.[8−16] The large state-dependent variation in the dipole moment causes a large Stokes' shift in both absorption and fluorescence spectra of these molecules, which are again very sensitive to the polarities of the solvents and the microenvironments.[8−16] Thus, a number of 7-aminocoumarin dyes have widely been used in studying solvatochromic properties, polarities of the microenvironments and to measure the solvent relaxation times (τ_s) using dynamic Stokes' shift method.[10−16]

The 7-aminocoumarin dyes are also good electron acceptors.[17−27] In the past few years a number of interesting observations have been made in relation to the electron transfer (ET) dynamics using coumarin dyes as the electron acceptors.[17−27] From femtosecond fluorescence up-conversion measurements it has been observed that in electron donating solvents, such as aniline, substituted anilines, hydrazines, etc., the fluorescence lifetimes (τ_f) of the coumarin dyes are drastically reduced in comparison to their lifetimes in other noninteracting solvents.[19−24] Correlating with the redox potentials of the coumarin dyes and the donor solvent molecules, this drastic reduction in the τ_f values of the coumarin dyes in the electron donating solvents have been attributed to ultrafast intermolecular ET from the solvent molecules to the excited dye molecules.[19−24] The donor−acceptor interactions between 7-aminocoumarin dyes and different amine donors have also been investigated by us in a noninteracting polar solvent, acetonitrile, using both steady-state and time-resolved fluorescence quenching measurements under diffusive condition.[25−27] It has been observed that the bimolecular quenching constants correlate well with the redox potentials of the donor−acceptor systems used, supporting the ET mechanism.[25−27] Though in all these studies[17−27] the ET has been predicted for the observed fluorescence quenching, direct evidence for the ET mechanism could not be established unambiguously mostly because the reduced radical characteristics of the coumarin dyes are not available in the literature.[25−27] In relation to the ultrafast ET from aniline solvents to excited

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10.1021/jp0203200 CCC: $22.00

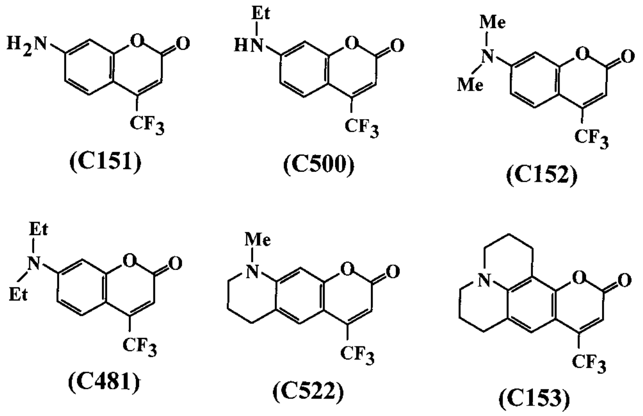


Figure 1. Chemical structures of the 7-aminocoumarins investigated in the present work. The abbreviations used in the present paper for these coumarin dyes are also given.

dye molecules, the only report that establishes ET mechanism is that of Kandori et al.,[28] where the transient species have been characterized by subpicosecond transient absorption studies on Nile blue-aniline system. For coumarin−amine systems, the nonavailability of the literature report on the coumarin reduced radical characteristics is one of the hurdle to establish ET mechanism unambiguously. In the present work our endeavor was to investigate the reduced radical characteristics of a series of 7-aminocoumarin dyes, which have been used extensively in the ET studies.[19−27] The chemical structures along with the abbreviations for the coumarin dyes used in the present work are shown in Figure 1.

2. Materials and Methods

Laser grade coumarin dyes were obtained from Lambda Physik, Kodak or Exciton and used as received. Organic solvents, namely, acetonitrile (ACN), 2-propanol (2PNL), and acetone (ACT), were of spectroscopic grade from Spectrochem India, and used without further purification. Nanopure water, having a conductivity of 0.1 μS cm^{-1}, was obtained by passing distilled water through a Barnstead nanopure water system. Aniline (AN) and triethylamine (TEA) were obtained from Spectrochem India and purified by distillation just before use. Since the coumarin dyes are almost insoluble in water, a mixed solvent (MS) system containing 5 mol dm^{-3} of 2PNL and 1 mol dm^{-3} of ACT in water was used in the present work as an alternative to the aqueous solvent. The pH of the solutions in MS was adjusted by using purest grade $HClO_4$ and NaOH, obtained from E. Mark, India. For all the experiments, the solutions were deaerated by purging high purity nitrogen gas (Iolar-2 grade from Indian Oxygen Ltd.) for about 10 min.

Ground-state absorption spectra were recorded with a Shimadzu UV−vis spectrophotometer, model UV-160A. The pH of the solutions in MS was measured using an Orion-901-A Ionalizer, fitted with a combination electrode. Pulse radiolysis (PR) experiments were carried out by irradiating the dye solutions in 1 cm × 1 cm quartz cuvettes with either 50 ns (for solutions in MS and in 2PNL) or 500 ns (for solutions in ACN) electron pulses from a 7 MeV Linear Electron Accelerator (LINAC, Ray Technology, England). The transients formed in the solution following the electron pulses were detected by kinetic spectrometric method using a 450 W pulsed xenon lamp as the monitoring light source. The radiation doses were measured by using aerated potassium thiocyanate dosimetry (5 × 10^{-2} mol dm^{-3} air saturated KSCN solution in water), following the maximum optical density (O. D.) of the $(SCN)_2^{\bullet-}$ radicals at 500 nm.[29]

The reduction potentials of the coumarin dyes (E_{red}) in MS were measured by cyclic voltammetric (CV) method using a Eco-Chemie Potentiostat/Galvanostat-20, with a GPES software. Solutions of the coumarin dyes (∼10^{-3} mol dm^{-3}) in MS containing 0.1 mol dm^{-3} potassium chloride as the supporting electrolyte were first deaerated by purging high purity N_2 gas for about 15 min. The CV measurements were then carried out using dropping mercury as the working electrode, graphite rod as the counter electrode and silver−silver chloride {Ag/AgCl/Cl$^-$(saturated); electrode potential is 0.197 V vs SHE}[30] as the reference electrode.

3. Results and Discussion

3.1. Pulse Radiolysis Studies in Aqueous−Organic Mixed Solvent (MS). The 7-aminocoumarin dyes investigated in the present work are not sufficiently soluble in water. In aqueous−organic MS (cf. section 2), however, the solubility of these dyes are increased substantially {∼(5−10) × 10^{-3} mol dm^{-3}}, making it possible to carry out the PR studies. For compounds which are not soluble in water but have good solubility in polar organic solvents, the MS system with the cosolvent compositions mentioned in section 2 has been established to be the best substitute for the aqueous solvent to carry out the pulse radiolytic reduction studies.[31−40]

In MS, since the major component is water, the primary radicals ($H^\bullet$, $OH^\bullet$, e_{aq}^-) formed following electron pulse are more or less similar to those produced in aqueous solution.[31,32] With 5 mol dm^{-3} of 2PNL and 1 mol dm^{-3} of ACT present in MS, these primary radicals are quantitatively converted to a common reducing radical, $(CH_3)_2\dot{C}OH$, via the following sequence of reactions.[31−41] When coumarin dyes (C) are also

$$H_2O \xrightarrow{\text{Irradiation}} H^\cdot,\ OH^\cdot,\ e_{aq}^- \tag{1}$$

$$H^\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2 \tag{2}$$

$$OH^\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O \tag{3}$$

$$e_{aq}^- + (CH_3)_2C{=}O \longrightarrow (CH_3)_2\dot{C}O^- \tag{4}$$

$$(CH_3)_2\dot{C}O^- + H_2O \longrightarrow (CH_3)_2\dot{C}OH + OH^- \tag{5}$$

present in the solution with a reasonable concentration (≥ 10^{-4} mol dm^{-3}), the dye molecules can undergo reduction by the $(CH_3)_2\dot{C}OH$ radicals due to the following one-electron-transfer reaction (eq 6).

$$C + (CH_3)_2\dot{C}OH \rightarrow C^{\bullet-} + (CH_3)_2CO + H^+ \tag{6}$$

Though in reaction 6 the reduced coumarin radicals have been represented in their anionic form, $C^{\bullet-}$, these radicals can also be converted to the corresponding protonated form, $CH^\bullet$, depending on the acid dissociation constants (pK_a^R; eq 7) of the latter radicals and the pH of the solution.

$$CH^\bullet \overset{pK_a^R}{\rightleftharpoons} C^{\bullet-} + H^+ \tag{7}$$

The transient absorption spectra for all the 7-aminocoumarin dyes in neutral MS solutions were recorded following 50 ns, 7 MeV electron pulses, keeping the irradiation dose about 16 Gy. The coumarin concentrations used in these experiments were about 2 × 10^{-4} mol dm^{-3}. For all the coumarin dyes, it was observed that the transient absorption grows for a time scale of

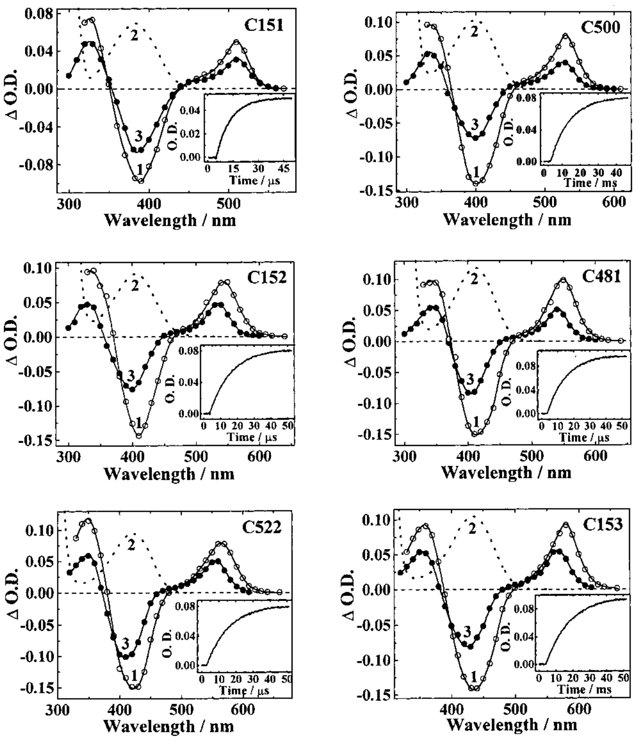


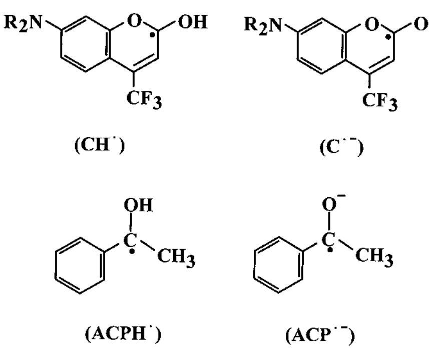
Figure 2. Transient absorption spectra obtained in aqueous−organic mixed solvent system (spectra 1) and in 2-propanol (spectra 3) following pulse radiolysis of the 7-aminocoumarins. The radiation doses used for these experiments were about 16 Gy. The ground-state absorption spectra of the coumarin dyes in MS are shown by spectra 2. The kinetic traces showing the formation of the transients are shown in the insets of the figure, measured at the longer wavelength absorption peak of the respective transients.

about 80 μs and the shape of the time-resolved transient absorption spectra remains unchanged for the whole time-scale of ∼0−80 μs. Figure 2 shows the transient absorption spectra for different coumarin dyes obtained at ∼80 μs delay (spectra 1) following the electron pulses. Typical kinetic traces showing the transient formation for different coumarin dyes are shown in the insets of Figure 2.

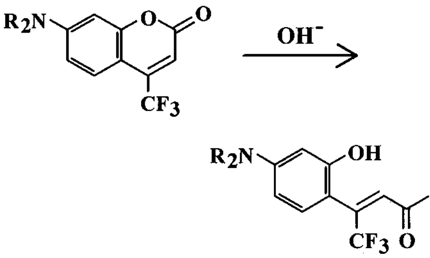
It is seen from Figure 2 that the transient absorption spectra for all the coumarin dyes have the following common features. There is a strong absorption band in the longer wavelength region of ∼500−700 nm. The peak position for this band gradually shifts toward longer wavelengths as the 7-amino group of the dyes becomes bulkier with alkyl- or cycloalkyl substituents. For all the coumarin dyes, there is a strong negative absorption band in the 380−500 nm region—the spectral region where the parent coumarin dyes investigated have strong ground-state absorption. For comparison the ground-state absorption spectra of the coumarin dyes in MS are also shown by spectra 2 in Figure 2. We thus infer that the negative absorption band in the 380−500 nm region arises due to the depletion of the parent dye molecules following their reduction by $(CH_3)_2\dot{C}OH$ redicals. In the transient spectra, there is also a strong absorption band at the shorter wavelength region of ∼320−380 nm. The peak position of this band is also seen to shift gradually toward longer wavelengths as the bulkier substituents are introduced at the 7-amino group of the dyes.

From the kinetic traces and the time-resolved transient absorption spectra obtained in MS it is indicated that for all the coumarin dyes only a single transient species is formed. Considering reactions 6 and 7, the transient species thus formed can exist as either of the two prototropic forms, namely, the

CHART 1



anionic form $C^{\bullet-}$ and the neutral form $CH^{\bullet}$. To characterize the actual prototropic form of the radicals formed in MS, the PR experiments of the coumarin dyes were carried out at different pH conditions. Interestingly it was seen that for a wide pH range of ∼1−9, the transient spectra remained unchanged. It is thus indicated that the coumarin reduced radicals exist in the same prototropic form in MS for the pH range of 1−9. Thus no prototropic equilibrium (eq 7) exists for these radicals in the pH range of ∼1−9. To be mentioned here that the reduced radical characteristics of the coumarin dyes could not be investigated in MS for solutions having pH > 9 as these molecules undergo hydrolysis at strongly alkaline conditions (reaction 8).



(8)

Since there is no prototropic equilibrium (eq 7) existing for the reduced coumarin radicals in the pH range of 1−9, and also since the reduced radicals characteristics could not be investigated in much stronger alkaline solutions, it was not possible to unambiguously ascertain the prototropic form of the reduced coumarin radicals formed in MS. However, considering the possible chemical structures of $CH^{\bullet}$ and $C^{\bullet-}$ radicals (cf. Chart 1), it is evident that the coumarin reduced radicals should resemble closely with the typical ketyl radicals.[42,43] For comparison, the chemical structures of the two prototropic forms of the acetophenone (ACP) ketyl radicals ($ACPH^{\bullet}$ and $ACP^{\bullet-}$ respectively) are also shown in Chart 1. It is thus expected that the acid−base characteristics of the reduced coumarin radicals will be quite similar to those of the other ketyl radicals. Since for most of the ketyl radicals, the pK_a^R values are in the range of 12−13,[44−47] we expect that the pK_a^R values of the reduced coumarin radicals could also be in the similar range. Thus, the reduced coumarin radicals formed in MS in the pH range of ∼1−9 are supposed to be in their $CH^{\bullet}$ form.

3.2. Pulse Radiolysis Studies in 2-Propanol (2PNL). To supplement the results obtained in MS, we also carried out the PR experiments in 2PNL solutions. On irradiation of deaerated 2PNL by high energy electron pulses, the acetone ketyl radicals, $(CH_3)_2\dot{C}OH$, are formed as the unique reducing radicals in the solution,[33−40] via the following sequence of reactions, where $\{(CH_3)_2CHOH\}^{**}$ represents the higher excited states of the solvent molecules. When coumarin dyes are also present in the

$$(CH_3)_2CHOH \overset{\text{Irradiation}}{\rightsquigarrow} \{(CH_3)_2CHOH^+ + e^-\}, \{(CH_3)_2CHOH\}^{**} \quad (9)$$

$$\{(CH_3)_2CHOH^+ + e^-\} \xrightarrow{\textbf{CR}} \{(CH_3)_2CHOH\}^{**} \quad (10)$$

$$\{(CH_3)_2CHOH\}^{**} \longrightarrow H^{\cdot} + (CH_3)_2\dot{C}OH \quad (11)$$

$$H^{\cdot} + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2 \quad (2)$$

solution with a reasonable concentration, the reduced radicals of these dyes are expected to be formed by reaction 6, exactly in the similar manner as in MS. However, unlike in MS, it is expected that in 2PNL the prototropic form of these radicals should be the CH$^\bullet$, as the ionic species H$^+$ and C$^{\bullet-}$ will be quite unstable in comparison to the neutral radical CH$^\bullet$ in an organic solvent like 2PNL. In fact, in pulse radiolytic reduction studies of many organic molecules in 2PNL, it has been observed that the radicals species are preferentially formed in the neutral form, even when the pK_a^R values of these species are substantially low (p$K_a^R \leq 2$).[33-40] Thus, in 2PNL the reduction of the coumarin dyes by (CH$_3$)$_2\dot{C}$OH radicals is supposed to occur as reaction 12.

$$C + (CH_3)_2\dot{C}OH \rightarrow CH^\bullet + (CH_3)_2CO \quad (12)$$

The transient absorption spectra obtained in the PR of the coumarin dyes in 2PNL are also shown by spectra 3 in Figure 2 along with those obtained in MS (spectra 1). From a comparison of the transient absorption spectra in 2PNL and MS, it is evident that in both the solvents the coumarin reduced radicals are formed in the same prototropic form. Since in 2PNL the reduced radicals are expected to be formed in the neutral form, CH$^\bullet$,[33-40] we infer that in MS also the radicals are formed in the same CH$^\bullet$ form for the whole pH range of ~1−9.

It is indicated from the PR results in 2PNL and MS that the C$^{\bullet-}$ form of the coumarin reduced radicals are very prone toward protonation (cf. reaction 7). Since the shape of time-resolved transient absorption spectra remained unchanged for the whole time-scale of formation (~0−80 μs) of these transients, it is indicated that the protonation of C$^{\bullet-}$ (cf. reaction 7) occurs much faster compared to the ET step (reaction 6) in both MS and 2PNL solutions. Present results also indicate that the protonation of C$^{\bullet-}$ is faster than the ET step even in alkaline MS solution with pH ~9. Since water is a major component in MS, we expect that in alkaline solutions the protonation of C$^{\bullet-}$ occurs mainly via the abstraction of a proton from a nearby water molecule rather than by a direct reaction of H$^+$ ion with the C$^{\bullet-}$ radical. Thus in alkaline MS solution the reduction of the coumarin dyes by (CH$_3$)$_2\dot{C}$OH radicals is predicted to occur by the following sequence of reactions.

$$C + (CH_3)_2\dot{C}OH + OH^- \rightarrow C^{\bullet-} + (CH_3)_2CO + H_2O \quad (13)$$

$$C^{\bullet-} + H_2O \rightarrow CH^\bullet + OH^- \quad (14)$$

We note that a similar protonation of the reduced radical anion in alkaline MS solution was also observed earlier by us in the pulse radiolytic reduction studies of a phenazine based dye, neutral red.[40]

To further supplement the results obtained in 2PNL and MS, we also carried out the PR experiments of the coumarin dyes in 2PNL solutions in the presence of ~1 mol dm^{-3} of a strong proton acceptor, namely, triethylamine (TEA). The transient absorption spectra obtained in these studies (not shown in the figure) were very similar to those obtained in 2PNL solutions in the absence of TEA. It is thus indicated that the C$^{\bullet-}$ radicals are much stronger proton acceptors than TEA. Since the pK_b value of TEA is 3.19,[48] present results indicate that the pK_a^R values of the CH$^\bullet$ radicals must be higher than ~11. Such a high pK_a^R value for the CH$^\bullet$ radicals is also expected considering the similarities in the structures of the present radicals with those of the typical ketyl radicals (cf. section 3.1).

It is evident from the results in 2PNL and MS that the CH$^\bullet$ form of the coumarin reduced radicals are invariably formed in both the solvents following the electron pulse irradiation. Since the pK_a^R values of the CH$^\bullet$ radicals are very high ($\geq$ 11), the initially formed C$^{\bullet-}$ radicals quickly undergo protonation in both 2PNL and MS. Thus the C$^{\bullet-}$ form of the radicals could not be stabilized and consequently the characteristics of these radicals could not be investigated in either 2PNL or MS solutions. To overcome the protonation problem of the C$^{\bullet-}$ radicals, we carried out the PR experiments of the coumarin dyes in acetonitrile (ACN) solutions, using a judicially designed experimental condition. Results of these experiments are discussed latter in section 3.5.

3.3. True Absorption Spectra of the CH$^\bullet$ Radicals in MS and in 2PNL. It is seen from Figure 2 that in the observed transient spectra there is a large negative absorption in the 380−500 nm region due to the depletion of the parent dye molecules. Thus to obtain the true absorption spectra of the CH$^\bullet$ radicals, it is essential to correct these observed spectra for the depleted dye concentrations. This was done using the following equation,[33-40]

$$\epsilon_R(\lambda) = \epsilon_P(\lambda) + \frac{\Delta OD(\lambda) G\{(SCN)_2^{\bullet-}\}\epsilon\{(SCN)_2^{\bullet-}\}}{\Delta OD\{(SCN)_2^{\bullet-}\}G(R)} \quad (15)$$

where $\epsilon_R(\lambda)$ and $\epsilon_P(\lambda)$ are the molar extinction coefficients of the CH$^\bullet$ radicals and the ground state of the coumarin dyes, respectively, at wavelength λ, ΔOD(λ) is the observed transient O.D. at the same wavelength, $G(R)$ is the G value of the CH$^\bullet$ radical formation, $G\{(SCN)_2^{\bullet-}\}$ is the G value for the (SCN)$_2^{\bullet-}$ radical formation in the dosimeter solution, $\epsilon\{(SCN)_2^{\bullet-}\}$ is the molar extinction coefficients of the (SCN)$_2^{\bullet-}$ radical at 500 nm, and $\Delta OD\{(SCN)_2^{\bullet-}\}$ is the observed maximum O.D. in the dosimeter solution for the (SCN)$_2^{\bullet-}$ radicals immediately after the electron pulse. In using eq 15, the G$\{(SCN)_2^{\bullet-}\}$ value was taken to be 2.9 and $\epsilon\{(SCN)_2^{\bullet-}\}$ value was taken to be 7.1 × 10^3 dm^3 mol^{-1} cm^{-1}.[29] The $G(R)$ values for the MS and 2PNL media were taken to be 6.2 and 5.1, respectively.[31,33-40] The true absorption spectra of the CH$^\bullet$ radicals thus obtained in MS and 2PNL solutions for different coumarin dyes are shown in Figure 3. It is seen from this figure that the CH$^\bullet$ radicals are having two strong absorption bands, one in the shorter wavelength region of about 300−400 nm and the other in the longer wavelength region of about 500−620 nm. The absorption maxima (λ_{abs}^{max}) and the corresponding molar extinction coefficients (ϵ_{abs}^{max}) of the CH$^\bullet$ radicals are listed in Table 1. It is seen that λ_{abs}^{max} values of the CH$^\bullet$ radicals gradually shift toward longer wavelengths as the 7-amino group of the dyes becomes bulkier. Further, the absorption maxima of the CH$^\bullet$ radicals are also seen to undergo a small red shift in MS in comparison to those in 2PNL solution, probably due to the higher solvent polarity in MS than in 2PNL.

3.4. Formation and Decay Kinetics of the CH$^\bullet$ Radicals in MS and 2PNL. The formation rates of the CH$^\bullet$ radicals in both 2PNL and MS were estimated from the kinetic traces

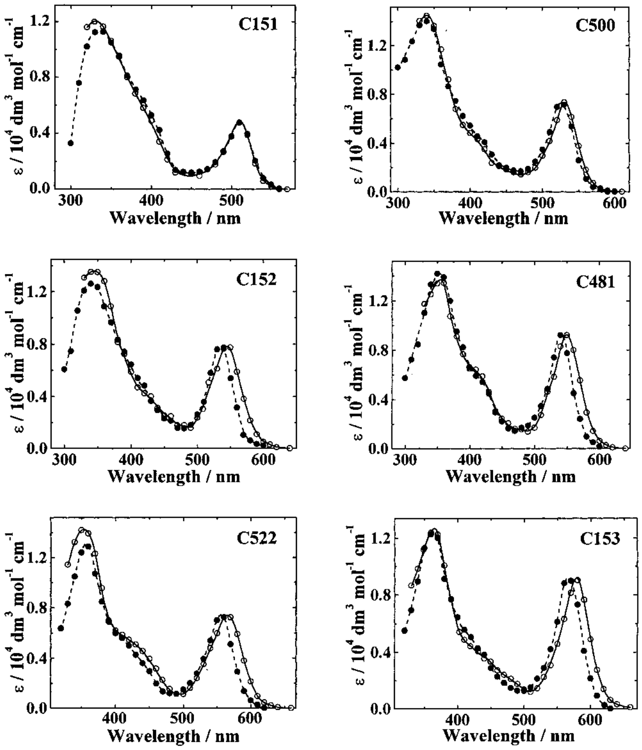


Figure 3. True absorption spectra of the CH$^•$ radicals of the coumarin dyes in aqueous−organic mixed solvent (○) and in 2-propanol (●) solutions, as obtained after correction of the observed transient spectra using eq 15.

TABLE 1: Absorption Characteristics of the Protonated Form of the Coumarin Reduced Radicals (CH$^•$) in 2-Propanol (2PNL) and Aqueous−Organic Mixed Solvent (MS) Systems

	λ_{abs}^{max}/nm		ϵ_{abs}^{max}/dm^{3}mol^{-1}cm^{-1}	
radicals species	2PNL	MS	2PNL	MS
C151H$^•$	325	325	11 300	12 050
	510	510	4 800	4 800
C500H$^•$	340	340	14 050	14 500
	525	530	7 300	7 400
C152H$^•$	340	345	12 700	13 600
	535	545	7 900	7 900
C481H$^•$	350	355	14 200	13 700
	540	550	9 250	9 250
C522H$^•$	360	355	13 150	14 300
	555	565	7 400	7 400
C153H•	360	365	12 550	12 750
	565	580	9 200	9 200

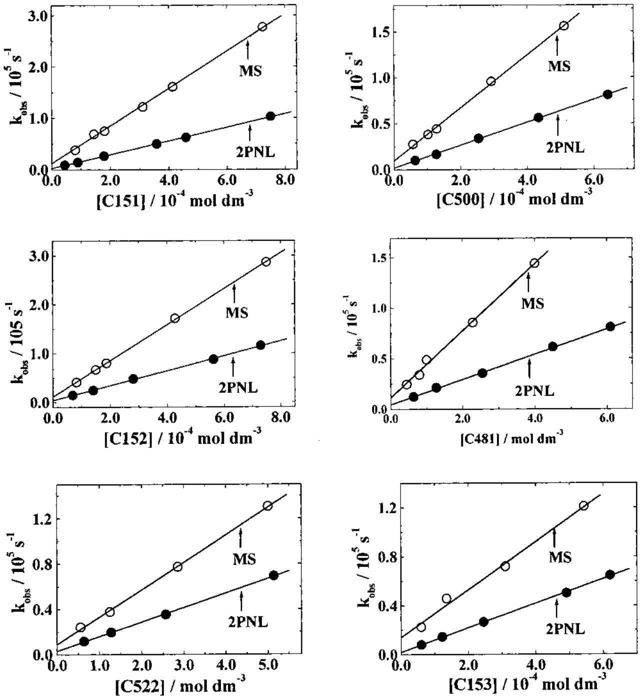


Figure 4. Variation of the observed first order formation rate constants (k_{obs}) of the CH$^•$ radicals versus the concentration of the coumarin dyes in aqueous−organic mixed solvent (○) and in 2-propanol (●) solutions. Within experimental error the plots are linear.

TABLE 2: Reduction Potentials of the Coumarin Dyes (E_{Red}) and the Bimolecular Formation Constants (k_f) of the CH$^•$ Radicals in 2-Propanol (2PNL) and Aqueous−Organic Mixed Solvent (MS) Systems

		k_f/10^8 dm^3 mol^{-1} s^{-1})	
compound/species	E_{red}/V^a	2PNL	MS
C151	−1.364	1.31	3.64
C500	−1.370	1.24	3.23
C152	−1.370	1.49	3.68
C481	−1.380	1.43	3.33
C522	−1.389	1.28	2.41
C153	−1.408	1.01	1.96

[a] The E_{red} values are against Ag/AgCl/Cl$^-$(saturated) electrode (reference potential 0.197 V vs SHE)[30] in MS system.

obtained mainly at the longer wavelength transient absorption bands (500−620 nm), to avoid the complications arising due to the ground-state absorption of the coumarin dyes below ~500 nm. It is seen that in both 2PNL and MS the formation of the CH$^•$ radicals follows a pseudo first-order kinetics. The observed first order formation rate constants (k_{obs}) are found to be the linear function of the coumarin concentrations used.

$$k_{obs} = k_f[C] + \text{constant} \tag{16}$$

The bimolecular formation constants (k_f) for the CH$^•$ radicals in both the solvents were thus obtained from the slopes of the k_{obs} vs [C] plots shown in Figure 4. The k_f values thus obtained for different CH$^•$ radicals in MS and 2PNL are listed in Table 2. It is seen from Table 2 that the CH$^•$ radicals of the dyes are formed with rates much lower than the typical diffusion controlled rates ($k_d \approx 1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) observed in solution phase.[49] Further, the k_f values in 2PNL are always about 2−3 times lower than those in MS.

Since the reduction of the coumarin dyes by $(CH_3)_2\dot{C}OH$ radical is effectively an ET process, it is interesting to see if the k_f values correlate with the reduction potentials (E_{red}) of the coumarin dyes. The E_{red} values of the coumarin dyes in MS were estimated in the present work using cyclic voltammetric technique and are listed in Table 2. Figure 5A,B show the ln(k_f) vs E_{red} plots for different coumarin dyes in MS and 2PNL solutions, respectively. Though the experimental points are largely fluctuating, yet it is indicated from Figure 5 that k_f apparently increases linearly with an increase with E_{red} values. The reason for the large fluctuations in the k_f vs E_{red} plots shown in Figure 5 are not very clear to us. Tentatively, we feel that the ET process from $(CH_3)_2\dot{C}OH$ radicals to different coumarin dyes are somewhat dependent on the nature of the substituents in the latter. An experimental error of about 10% is also included in these results as are usually seen in the measurements using the present PR set up. The apparent linear trend in the k_f vs E_{red} plots shown in Figure 5 is expected to be quite normal for outer sphere ET reactions as are the present cases supposed to

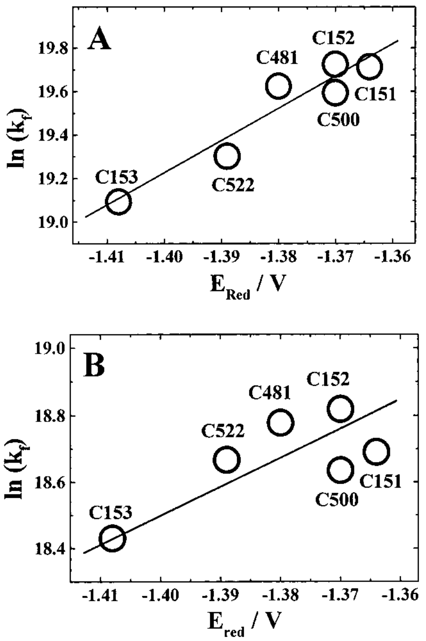


Figure 5. Variation of the bimolecular formation constant (k_f) of the CH$^{\bullet}$ radicals versus the reduction potential (E_{red}) of the coumarin dyes in aqueous−organic mixed solvent (A) and in 2-propanol (B) solutions. The ln(k_f) vs E_{red} plots are apparently linear though the experimental data points are quite largely fluctuating, probably due to the substituent effects of the coumarin dyes on the reaction kinetics.

be, because the range of E_{red} covered for the coumarin dyes studied is not that large and the k_f values are much lower than the diffusion controlled rate.

For all the coumarin dyes, their CH$^{\bullet}$ radicals are seen to be very long-lived in both 2PNL and MS solutions. In fact, no decay for the transients could be observed in 2PNL and in neutral and alkaline MS, for a time scale of about 5 ms. In acidic MS (pH ∼1), however, the CH$^{\bullet}$ radical absorption showed a very slow decay in the time scale of about 5 ms. These decay were, however, so slow that we could not analyze the kinetic traces with confidence to extract out the actual decay rate constants.

3.5. Pulse Radiolysis Studies of the Coumarin Dyes in Acetonitrile Solution. PR of the coumarin dyes in acetonitrile (ACN) solutions were carried out by judicially designing the experimental conditions to produce the C$^{\bullet-}$ form of the coumarin reduced radicals in the solution. As deaerated liquid ACN is irradiated with high-energy electron pulses, the solvent molecules initially undergo ionization, producing the solvent ion-pairs (ACN$^{+}\cdots$e^{-}) in the solution.[50] If no solute is present in

$$\mathrm{ACN} \xrightarrow{\text{Irradiation}} (\mathrm{ACN}^{+}\cdots e^{-}) \qquad (17)$$

the solution with a reasonable concentration (≥10^{-3} mol dm^{-3}), these ion pairs undergo very fast charge recombination (CR) reaction, producing back the solvent molecules.[50]

$$(\mathrm{ACN}^{+}\cdots e^{-}) \xrightarrow{\mathrm{CR}} \mathrm{ACN} \qquad (18)$$

In the present experiments, we used about 1.0 mol dm^{-3} aniline (AN) as the additive to scavenge the ACN^{+} ions from the ion pairs (ACN^{+} ⋯ e^{-}), and thus made available appreciable amount of e^{-} to reduce the coumarin dyes, the latter being kept in the millimolar concentrations. Under this experimental condition, following sequence of reactions take place following the electron pulse to produce the C$^{\bullet-}$ form of the radicals in the solution.

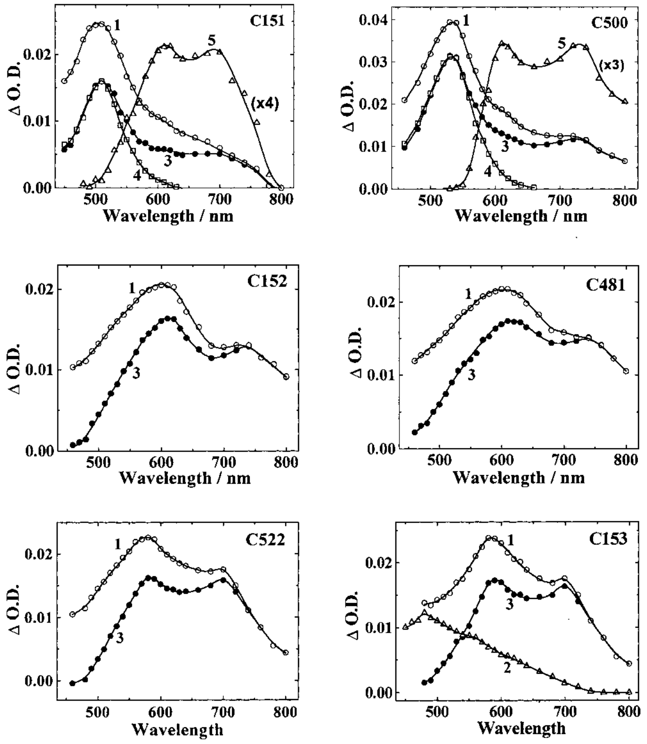


Figure 6. Transient absorption spectra 1 obtained in acetonitrile (ACN) solutions containing 1.0 mol dm^{-3} of aniline (AN) and 2 × 10^{-3} mol dm^{-3} of the coumarin dyes at a delay of 0.8 μs following electron pulse. The radiation doses used were about 45 Gy. Spectum 2 corresponds to that of AN$^{\bullet+}$ radical in ACN, obtained in solution containing only 1.0 mol dm^{-3} of AN. Spectra 3 represent those obtained by subtracting spectrum 2 from spectra 1. Spectra 4 correspond to those obtained in ACN solutions containing 1.0 mol dm^{-3} of triethylamine (TEA) and 2 × 10^{-3} mol dm^{-3} of the coumarin dyes. The spectra obtained after subtracting spectra 4 from spectra 3 are shown by spectra 5. For clarity, spectra 5 for C151 and C500 are shown in this figure after magnification by 4 and 3 times, respectively.

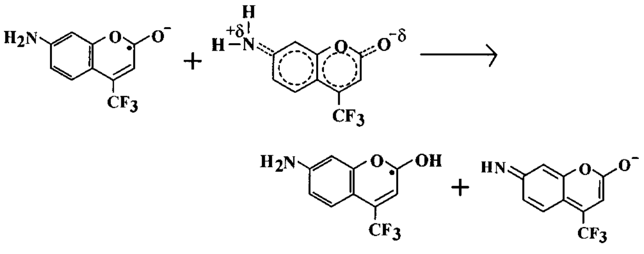
$$(\mathrm{ACN}^{+}\cdots e^{-}) + \mathrm{AN} \rightarrow \mathrm{ACN} + \mathrm{AN}^{\bullet+} + e^{-} \qquad (19)$$

$$\mathrm{C} + e^{-} \rightarrow \mathrm{C}^{\bullet-} \qquad (20)$$

Figure 6 shows the transient absorption spectra obtained in ACN solution containing 1.0 mol dm^{-3} of AN and 2 × 10^{-3} mol dm^{-3} of the coumarin dyes, at about 0.8 μs delay following the electron pulse (spectra 1), a time delay where the transients show the maximum absorption. Since these observed spectra are the summation of the absorption spectra of both C$^{\bullet-}$ and AN$^{\bullet+}$ radicals, we had to subtract the absorption spectrum of the latter from the observed spectra 1 in Figure 6 to obtain the spectra due to the C$^{\bullet-}$ radicals. In the present work the absorption spectrum of AN$^{\bullet+}$ radical was obtained at 0.8 μs delay after the electron pulse to a solution containing only 1.0 mol dm^{-3} of AN in ACN, as shown by spectrum 2 in Figure 6. The absorption spectra due to the C$^{\bullet-}$ radicals obtained by subtracting spectrum 2 from spectra 1 and are shown by spectra 3 in Figure 6.

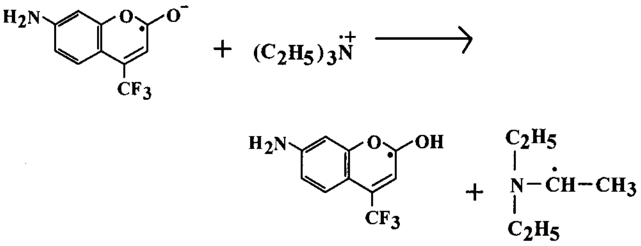
From spectra 3 in Figure 6 it is seen that the absorption characteristics of the C$^{\bullet-}$ radicals in ACN solution are completely different than those of the CH$^{\bullet}$ radicals observed in 2PNL and in MS solutions. For all the coumarin dyes except C151 and C500, the spectra obtained in ACN are quite broad, spreading for the wavelength range of ∼500−800 nm. For the wavelength range below ∼450 nm, we could not obtain the transient absorption spectra due to strong ground-state absorption of the coumarin dyes with a concentration of $\sim 2 \times 10^{-3}$ mol dm^{-3}. It is seen from spectra 3 in Figure 6 that the transient spectra for all the coumarin dyes (except C151 and C500) apparently show two absorption peaks, one around 585−615 nm region and the other around 700−740 nm region. The shape of these spectra thus obtained in ACN solutions are very similar to the transient absorption spectra obtained in our earlier picosecond laser flash photolysis (LPF) experiments in relation to the ET studies in coumarin-amine systems in ACN solutions.[25−27] Such a similarity in the transient absorption spectra obtained in the PR and LFP studies clearly indicate that the transients formed in ACN solutions following PR are the $C^{\bullet -}$ forms of the reduced coumarin radicals.

It is very interesting to note from Figure 6 that in the case of C151 and C500, the transient spectra 3 obtained in ACN solution are substantially different in shape than those obtained for the other coumarin dyes. Comparing spectra 3 in Figure 6 for C151 and C500 with the absorption spectra of the $CH^{\bullet}$ radicals in 2PNL and MS shown in Figures 2 and 3, it is indicated that some $CH^{\bullet}$ radicals might have also been formed for C151 and C500 in ACN solution, along with their anion radicals, $C^{\bullet -}$. In fact, the decay kinetics for the transients recorded at the shorter wavelength absorption band (460−550 nm) in ACN solutions are seen to be substantially different than those observed at the longer wavelength absorption band (600−800 nm). We thus infer that the 460−550 nm and the 600−800 nm transient absorption bands observed in ACN for C151 and C500 correspond to two different species. Structurally, C151 and C500 differ from rest of the coumarin dyes with respect to the presence of the NH hydrogen. Since the coumarin dyes in polar solvents (e.g. ACN) exist in their intramolecular charge transfer (ICT) structure,[51,52] a partial positive charge is developed at the 7-amino group of these dyes, making the NH hydrogen somewhat acidic. Since the $C^{\bullet -}$ radicals are having strong proton affinity (cf. sections 3.1 and 3.2), it is quite possible that a fraction of the $C^{\bullet -}$ radicals formed by reaction 20 undergoes a proton-transfer reaction with the parent dye molecules (reaction 21), resulting in the formation of some $CH^{\bullet}$ radicals in the solution.



(21)

To ascertain the above results, we also carried out the PR experiments of the coumarin dyes in ACN solutions in the presence of 1 mol dm^{-3} of TEA as the solvent cation scavenger. The transient absorption spectra obtained in these experiments are seen to be very similar to the $CH^{\bullet}$ radicals obtained in 2PNL solution and there is no absorption band in the 600−800 nm region corresponding to the $C^{\bullet -}$ form of the radicals. These results are along with our expectations as the $TEA^{\bullet +}$ radical cations formed by a reaction similar to 19 are strong proton donors.[53−56] Thus the $C^{\bullet -}$ radicals initially formed by reaction 20 in ACN solution will quickly undergo a fast proton-transfer reaction with $TEA^{\bullet +}$ (reaction 22) resulting in the formation of the $CH^{\bullet}$ radicals in the solution. Typical transient absorption spectra obtained for C151 and C500 in ACN solution in the presence of 1 mol dm^{-3} of TEA are shown as spectra 4 in Figure 6 after normalization at the 500−530 nm peaks for a comparison with the spectra obtained in ACN in the presence of AN. It is evident that the spectra obtained using TEA have only the 450−550 nm absorption band but the 600−800 nm bands corresponding to the $C^{\bullet -}$ radicals are absent. Thus we infer that the strong transient absorption band in the 450−500 nm region obtained for C151 and C500 in ACN solution with AN as the solvent cation scavenger is due to the formation of some $CH^{\bullet}$ radicals. The transient absorption band in the 600−800 nm region in ACN solution with AN as the additive is, however, due to the $C^{\bullet -}$ form of the coumarin reduced radicals, as are formed for all other coumarin dyes. To be mentioned here that with TEA as the additive, the transient absorption spectra obtained in ACN solution for the other coumarin dyes were also very similar to the $CH^{\bullet}$ radical absorption spectra obtained in 2PNL solutions.



(22)

3.6. True Absorption Spectra of the $C^{\bullet -}$ Radicals in ACN Solutions. The true absorption spectra of the $C^{\bullet -}$ radicals in ACN solutions were obtained by correcting the spectra 3 in Figure 6 using the following relation.

$$\epsilon_R(\lambda) = \epsilon_P(\lambda) + \frac{\Delta OD(\lambda)}{[C^{\bullet -}]} \qquad (23)$$

where $\epsilon_R(\lambda)$ and $\epsilon_P(\lambda)$ are the molar extinction coefficients of the $C^{\bullet -}$ radicals and the ground state of the coumarin dyes, respectively, at wavelength λ, $\Delta OD(\lambda)$ is the observed O.D. in the transient spectra at the same wavelength and $[C^{\bullet -}]$ is the concentration of the $C^{\bullet -}$ radicals formed in the solution. The $[C^{\bullet -}]$ values for all the coumarin dyes excluding C151 and C500 were estimated by assuming that the $C^{\bullet -}$ radicals are formed with the concentration as that of the $AN^{\bullet +}$ radical. Using the observed O.D. for $AN^{\bullet +}$ radical at 450 nm and the reported ϵ value for this species ($\epsilon = 4000$ dm^3 mol^{-1} cm^{-1} at 450 nm),[45,46] we estimated the concentration of $AN^{\bullet +}$ and consequently that of the $C^{\bullet -}$ radicals formed in ACN solution. Thus the ϵ_R values for the $C^{\bullet -}$ radicals for the spectral range of about 450−800 nm were obtained by correcting the spectra 3 in Figure 6 using relation 23. The corrected absorption spectra for the $C^{\bullet -}$ radicals of all the coumarin dyes excluding C151 and C500 thus obtained are shown in Figure 7. The absorption maxima (λ_{abs}^{max}) and the corresponding ϵ values (ϵ_{abs}^{max}) for the $C^{\bullet -}$ radicals are listed in Table 3. It is seen from this table that the $C^{\bullet -}$ radicals absorb at much longer wavelengths than the $CH^{\bullet}$ radicals and the absorptions due to $C^{\bullet -}$ radicals are relatively weaker compared to those of the $CH^{\bullet}$ radicals. At this point it is interesting to compare the true absorption spectra of the 7-aminocoumarin dyes shown in Figure 7 with the absorption spectrum of the anion radical of unsubstituted coumarin dye (1,2-benzopyrone)

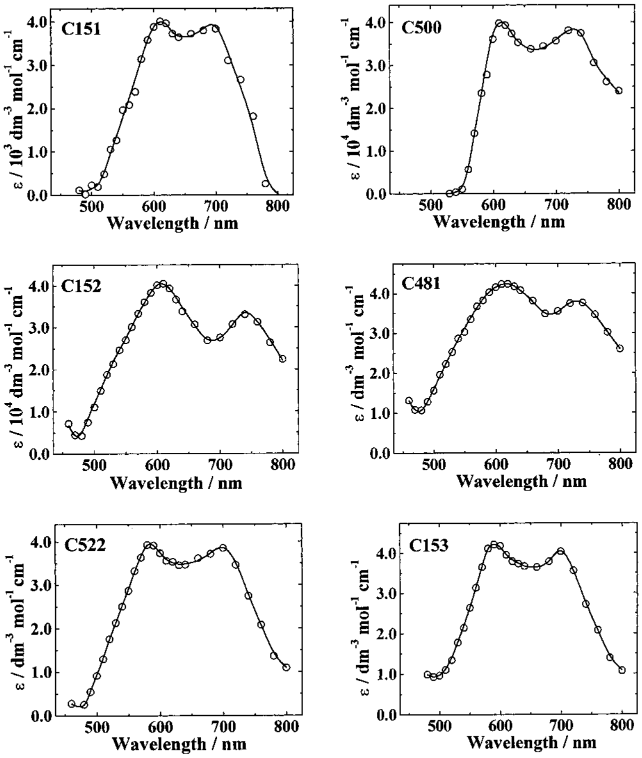


Figure 7. True absorption spectra of the C$^{\bullet-}$ radicals of the coumarin dyes in acetonitrile solutions, as obtained after correction of the observed transient spectra using eq 23.

TABLE 3: Absorption Characteristics of the Anionic Form of the Coumarin Reduced Radicals (C$^{\bullet-}$) in Acetonitrile (ACN) Solutions

radical species	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$/nm	$\epsilon_{\mathrm{abs}}^{\mathrm{max}}$/dm^{3}mol^{-1}cm^{-1}
C151$^{\bullet-}$	615, 690	4000, 3940
C500$^{\bullet}$	615, 730	4000, 3840
C152$^{\bullet-}$	610, 740	4060, 3350
C481$^{\bullet-}$	615, 730	4260, 3810
C522$^{\bullet-}$	585, 700	3960, 3840
C153$^{\bullet-}$	590, 700	4220, 4050

at low-temperature MTHF matrix as reported by Shida.[46] It is seen that the spectrum for the coumarin anion radical reported by Shida has a broad absorption band in the 500−800 nm region, with a peak at around 648 nm. Apparently this reported spectrum of the coumarin anion radical at low temperature is qualitatively very similar to the ones obtained for the anion radicals of the 7-aminocoumarin dyes in the present work, having broad absorption bands in the 500−800 nm region. Further, the molar extinction coefficient for the coumarin anion absorption as reported by Shida is seen to be very low with $\epsilon_{\mathrm{abs}}^{\mathrm{max}}$ only in the range of about 3000 dm^3 mol^{-1} cm^{-1}. We also note that the $\epsilon_{\mathrm{abs}}^{\mathrm{max}}$ values for the anion radicals of the present 7-aminocoumarin dyes are found to be very low, in the range of only about 4000 dm^3 mol^{-1} cm^{-1}. From a comparison of the present results with the reported results of Shida on the coumarin anion radical spectrum, it is evident that the transient intermediates formed in the PR of the 7-aminocoumarin dyes in ACN solution must be the C$^{\bullet-}$ radicals of the dyes. It is also indicated from the present results that the C$^{\bullet-}$ form of the coumarin radicals absorb much weaker in comparison to their protonated form CH$^{\bullet}$.

For C151 and C500 dyes, since both C$^{\bullet-}$ and CH$^{\bullet}$ forms of the radicals are formed simultaneously in ACN solution, it was not straightforward to obtain the true absorption spectra for their C$^{\bullet-}$ radicals. Thus for these two dyes, the normalized transient spectra 4 in Figure 6 for C151 and C500 was first subtracted from spectra 3 in the same figure to obtain the absorption spectra only due to the C$^{\bullet-}$ radicals of the two dyes. The spectra for the C$^{\bullet-}$ radicals of C151 and C500 thus obtained are shown by spectra 5 in Figure 6. Since the concentration of the C$^{\bullet-}$ radicals corresponding to these spectra are not known, we tentatively used an $\epsilon_{\mathrm{abs}}^{\mathrm{max}}$ value of 4000 dm^3 mol^{-1} cm^{-1} for the 615 nm absorption peak for both C151$^{\bullet-}$ and C500$^{\bullet-}$ radicals, an average $\epsilon_{\mathrm{abs}}^{\mathrm{max}}$ value obtained for the other C$^{\bullet-}$ radicals for the corresponding absorption peak (cf. Table 3). Thus the concentrations for [C151$^{\bullet-}$] and [C500$^{\bullet-}$] corresponding to spectra 5 in Figure 6 were estimated from the O. D. values at 615 nm peak for the two radicals. Using these C$^{\bullet-}$ concentrations, the spectra 5 in Figure 6 were corrected following eq 23 to obtain the true absorption spectra for the C151$^{\bullet-}$ and C500$^{\bullet-}$ radicals and are shown in Figure 7. It is seen from Figure 7 that the C$^{\bullet-}$ radicals for all the coumarin dyes have very similar absorption characteristics, showing two broad absorption bands in the 500−800 nm region. The extinction coefficients for these absorption bands for the C$^{\bullet-}$ radicals are seen to be much weaker compared to those of the CH$^{\bullet}$ radicals obtained in 2PNL and MS solutions.

In ACN solution, the C$^{\bullet-}$ form of the reduced coumarin radicals are seen to undergo a slow second-order decay with rate constants (2*k*) in the order of ∼(1−2) × 10^7 dm^3 mol^{-1} s^{-1}. The details of the decay mechanism, however, could not be investigated in the present work.

4. Conclusion

The reduced radical characteristics of a series of 7-aminocoumarin dyes have been investigated in aqueous−organic mixed solvent (MS), 2-propanol (2PNL) and acetonitrile (ACN) solutions using pulse radiolysis (PR) technique. It is seen that in MS, the neutral form of the reduced radicals (CH$^{\bullet}$) are formed for a wide pH range of ∼1−9 following the electron pulse. Since the coumarin dyes undergo hydrolysis at strongly alkaline solutions (pH > 10), it was not possible to estimate the pK_a^R values of the CH$^{\bullet}$ radicals. In 2PNL also, the reduced radicals of the coumarin dyes are seen to form in the CH$^{\bullet}$ form. Using a strong proton acceptor like triethylamine (TEA; pK_b = 3.19) in 2PNL solution also cannot resist the protonation of the initially formed C$^{\bullet-}$ radicals, indicating that the pK_a^R values of the CH$^{\bullet}$ radicals are higher than about 11. Thus the C$^{\bullet-}$ form of the reduced coumarin radicals appears to be very affinic toward proton in both 2PNL and MS solutions. The C$^{\bullet-}$ form of the radicals of the coumarin dyes could, however, be produced unambiguously in acetonitrile solutions, by carrying out PR experiments in the presence of ∼1 mol dm^{-3} of aniline (AN) as the solvent cation scavenger. The absorption spectra of the C$^{\bullet-}$ radicals are seen to be very broad and weak in comparison to those of the CH$^{\bullet}$ radicals. It is seen that in 2PNL and MS, the CH$^{\bullet}$ form of the radicals are very stable and show almost no decay for about 5 ms. In ACN solution, however, the C$^{\bullet-}$ form of the radicals undergo a slow second-order decay, with rate constant in the order of ∼(1−2) × 10^7 dm^3 mol^{-1} s^{-1}. Since the coumarin dyes are good electron acceptors for many intermolecular ET studies, present results will be very useful in characterizing the transient species formed following ET reactions and consequently in elucidating the ET mechanism in systems whereby the coumarin dyes are used as the electron acceptors.

Acknowledgment. The authors are thankful to Dr. R. I. Sundaresan and Mr. A. K. Satpati of Analytical Chemistry Division, BARC, for their kind help in the cyclic voltammetric measurements.

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