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A pulse radiolysis study of coumarin and its derivatives

Thounaojam S. Singh [a], B.S. Madhava Rao [a,*], Hari Mohan [b], Jai P. Mittal [b]

[a] *Department of Chemistry, National Centre for Free Radical Research, University of Pune, Pune 411007, India*
[b] *Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

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Abstract

The kinetics and the transient absorption spectra from the reactions of $^{\bullet}OH$, $O^{\bullet -}$, e_{aq}^{-} and $SO_4^{\bullet -}$ radicals with coumarin, 4-methyl-7-hydroxycoumarin, 7-methoxycoumarin and 6,7-dimethoxycoumarin in aqueous solutions were studied by pulse radiolysis with optical detection. The second-order rate constants for the reaction of the $^{\bullet}OH$ radical with coumarin was found to be $6.4 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$ and the introduction of different substituents to coumarin did not have any significant effect on the rates. The rate constants for the reaction of the hydrated electron, however, decreased with the introduction of the electron donating groups. The transient absorption spectra of the $^{\bullet}OH$ adducts of coumarin and its derivatives have λ_{max} at 360–370 and 425–460 nm. In the case of 4-methyl-7-hydroxycoumarin, the $^{\bullet}OH$ adduct undergoes dehydration leading to phenoxyl radical. The radical cation of coumarin formed by electron transfer in the $SO_4^{\bullet -}$ reaction is hydrolysed to yield the $^{\bullet}OH$ adducts. The radical cation is stabilised in methoxy derivatives or undergoes deprotonation to give phenoxyl radical in 4-methyl-7-hydroxycoumarin. The initially formed radical anion of coumarin and its derivatives formed in the reaction of the hydrated electron is protonated very fast ($k \geq 10^7\,s^{-1}$). The neutral electron adduct of coumarin ($\lambda_{max} = 360$ nm) is finally transformed by 1,2-H shift ($k = 2.7 \times 10^4\,s^{-1}$) into a thermodynamically more stable oxygen centred radical.
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Keywords: Pulse radiolysis; Kinetics; Transient absorption spectra; Coumarin

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1. Introduction

Radiation chemical reactions of the primary radicals of water radiolysis ($^{\bullet}OH$, e_{aq}^{-} or $H^{\bullet}$) and secondary radicals ($N_3^{\bullet}$, $SO_4^{\bullet -}$, $Cl_2^{\bullet -}$ or $Br_2^{\bullet -}$, etc.) derived from them with benzenes and its monosubstituted derivatives in aqueous solution have been widely studied [1–16] and these studies have contributed significantly to our understanding of their reactivity and its correlation with the structure.

The $^{\bullet}OH$ radical has been shown to react with substituted benzenes by addition to the aromatic ring forming a π complex which then rearranges to a Wheland intermediate (σ complex) leading to the formation of different isomeric $^{\bullet}OH$ adducts. The reactions of oxidising species such as $N_3^{\bullet}$, $SO_4^{\bullet -}$, $Cl_2^{\bullet -}$ or $Br_2^{\bullet -}$ with substituted benzenes result in the formation of the radical cation. Among them, the $SO_4^{\bullet -}$ radical anion ($E^{\circ} = 2.43$ V versus NHE) [17] and $N_3^{\bullet}$ ($E^{\circ} = 1.33$ V versus NHE) [17] are commonly used. These radicals react with aromatic compounds by an electron transfer mechanism from the benzene ring leading to the formation of the radical cation which then either deprotonates in the case of compounds having ionisable proton, or undergoes hydrolysis to give the corresponding OH adducts.

We have earlier reported [18–23], the radiation chemical oxidation of disubstituted benzenes of the type $C_6H_{5-n}X_nY$, where X is a halogen and Y = NH_2, Cl, Br, CH_3, CH_2Cl, CF_3 or OCH_3. These studies have been helpful in establishing the $^{\bullet}OH$ radical reaction mechanism in terms of the activation/deactivation effects of the electron donating/electron withdrawing substituents. In combination with the product analysis data, the relative reactivities for the $^{\bullet}OH$ radical attack at different carbon positions of cresols and chlorotoluenes were determined from the pulse radiolysis studies [22]. Based on the Hammett analysis, ρ^{+} values of -0.5 for the $^{\bullet}OH$ radical reaction and -1.6 to -1.2 for the reaction of $SO_4^{\bullet -}$ were obtained indicating the difference in the reaction mechanism between the two reacting species [20].

The reactivity of the hydrated electron with benzenes and its derivatives is usually low except in the case of compounds containing COOH [24], NO_2 [25,26], CHO [27] or halogen [26]. In benzoic acid [24], the electron adduct transient species have pK_a values of 5.3 and 12.0. Similarly, in chlorobenzaldehyde [26], the initially formed transient species exists in the deprotonated form above pH 8.2. In contrast, the electron adduct of the purine derivatives [28–31]

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* Corresponding author. Tel.: +91-20-569083; fax: +91-20-5651728.
E-mail address: bsmr@chem.unipune.ernet.in (B.S. Madhava Rao).

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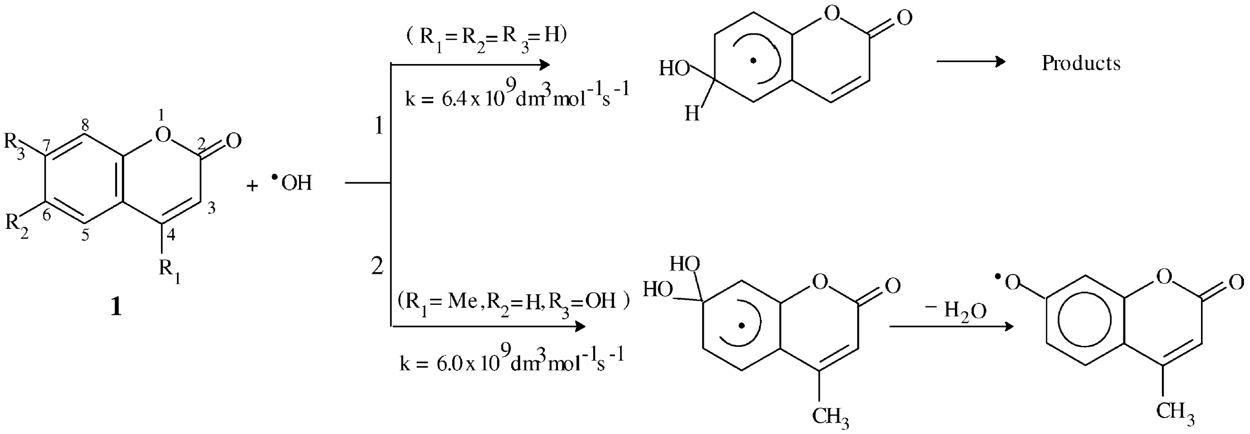


Scheme 1. Proposed mechanism of the reaction of the •OH radical with coumarin.

are protonated very fast and the initial spectrum is assigned to the hetero atom protonated carbon centred radical. This radical is finally gets transformed into a carbon protonated hetero atom centred radical.

Since organic acids like benzoic acid [24], acrylic acid [32], cinnamic acid [32] are in the deprotonated form at normal pH, it is not possible to examine whether the protonation of the initially formed mono radical anion occurs in the reaction of the e_{aq}^- with these compounds. Since coumarin (structure **1**, Scheme 1) does not have an ionisable hydrogen, this aspect can be studied without any ambiguity. Furthermore, it is interesting to examine whether tautomerisation reaction as observed in purines occurs in coumarin. Coumarin, the condensed product of *o*-hydroxycinnamic acid, is an interesting compound to investigate the protonation–deprotonation equilibrium as observed in purines.

Earlier studies on coumarin were limited to the product analysis by gamma radiolysis [33] and its reaction with hydrated electron [34] by pulse radiolysis. In this work, the results from the study of the reactions of •OH, $O^{\bullet -}$, e_{aq}^- and $SO_4^{\bullet -}$ with coumarin, 7-methoxycoumarin, 6,7-dimethoxycoumarin and 4-methyl-7-hydroxycoumarin are reported to investigate the effect of electron donating/electron withdrawing substituents with a view to gain further insight into the reaction mechanism.

2. Experimental

Coumarin and its derivatives are a gift from our Organic Chemistry Division and their synthesis was reported earlier [35]. Their purity was found to be >98% and were used without any further purification. Other chemicals used were of analytical grade. The solutions were prepared in Millipore–Milli Q filtered water and were saturated with appropriate gases before the dissolution of the solute to avoid its volatilisation during degassing. The pH of the solutions were adjusted by using analytical grade NaOH or $HClO_4$. High purity N_2 and N_2O gases of Indian Oxygen Ltd. were used for saturation. All experiments were carried out at room temperature (∼25 °C). For spectral studies, the [solute] was maintained at $5 \times 10^{-4}\,mol\,dm^{-3}$ while it was varied in the range $(1.0–5.0) \times 10^{-4}\,mol\,dm^{-3}$ for the measurement of kinetics. The reaction of the •OH radical was studied in N_2O saturated aqueous solutions where e_{aq}^- is quantitatively converted into the •OH radical (reaction (1)):

$$N_2O + e_{aq}^- \xrightarrow{H_2O} {}^{\bullet}OH + OH^- + N_2 \qquad (1)$$

The study of the $O^{\bullet -}$ reaction was carried out in N_2O saturated solutions at pH ∼13 using $0.1\,mol\,dm^{-3}$ NaOH. Under these basic conditions, more than 90% of the •OH radical essentially exists as $O^{\bullet -}$ (reaction (2)):

$${}^{\bullet}OH + OH^- \rightarrow O^{\bullet -} + H_2O \quad (pK_a = 11.9) \qquad (2)$$

The reactions of the hydrated electron were studied by irradiating N_2 saturated solutions of the substrate containing *tert*-butyl alcohol ($0.2\,mol\,dm^{-3}$) to scavenge the •OH radical.

The reaction of $SO_4^{\bullet -}$ was studied in N_2 saturated aqueous solutions containing $K_2S_2O_8$ ($1.5 \times 10^{-2}\,mol\,dm^{-3}$) and $0.2\,mol\,dm^{-3}$ *tert*-butyl alcohol. Under these reaction conditions, $SO_4^{\bullet -}$ radical is produced as shown in reaction (3):

$$S_2O_8{}^{2-} + e_{eq}^-(H) \rightarrow SO_4{}^{\bullet -} + SO_4{}^{2-}(HSO_4{}^-) \qquad (3)$$

Pulse radiolysis experiments were carried out using high-energy 7 MeV electron pulses (pulse width 50 ns) from a linear accelerator at the Bhabha Atomic Research Centre, Mumbai and the details of the set-up are reported elsewhere [36]. The KSCN dosimeter was used assuming $G(\varepsilon_{500}) = 21{,}500\,dm^3\,mol^{-1}\,cm^{-1}$ per 100 eV for the transient $(SCN)_2{}^{\bullet -}$. The dose used during the experiments was kept in the range 12–15 Gy/pulse. The transient absorption traces were recorded on a storage oscilloscope interfaced to a computer for the analysis of the kinetics.

Table 1
Second-order rate constants (k, 10^9 $dm^3\,mol^{-1}\,s^{-1}$), absorption maxima (λ_{max}, nm), and molar extinction coefficients (ε, $dm^3\,mol^{-1}\,cm^{-1}$) obtained in the reactions of $^{\bullet}OH$, $O^{\bullet -}$, e^-_{aq} and $SO_4{}^{\bullet -}$ with coumarin and derivatives

Compound	$^{\bullet}OH$			$O^{\bullet -}$		$SO_4{}^{\bullet -}$		e^-_{aq}		
	k	λ_{max}	ε	k	λ_{max}	k	λ_{max}	k	λ_{max}	ε
Coumarin	6.4	345 425	3600 2100	0.5	370 445	5.9	350	17.0 (2.7)	360	9800
4-Methyl-7-hydroxycoumarin	6.0	365	6700	0.6	465 490	5.6	360 580	13.1 (2.5)	365	11800
7-Ethoxycoumarin	6.5	370 460	1600 1300	1.7	365 490	5.8	365 585 625	14.2 (1.1)	380	10950
6,7-Dimethoxycoumarin	6.0	310	3350	n.d.		5.3	390 585	13.0 (4.9)	380	4050

The values in parentheses represent the first-order rate constants ($k/10$, ε^4, ε^{-1}) for the decay of the absorption maxima; n.d.: not determined.

3. Results and discussion

3.1. Kinetics

3.1.1. Reactions of $^{\bullet}OH$ and $O^{\bullet -}$

The rates of the reaction of the $^{\bullet}OH$ radical with coumarin, 7-methoxycoumarin, 6,7-dimethoxycoumarin and 4-methyl-7-hydroxycoumarin in neutral N_2O saturated solutions (pH: ~7.0) were determined by measuring the rates of the product formation at the respective absorption maxima lying in the range 310–370 nm. The absorption build-up measured at the λ_{max} was found to be continuous whose rates linearly increased with [solute] in the range $(1.0–5.0) \times 10^{-4}$ mol dm^{-3}. The second-order rate constants evaluated from the plots of k_{obs} versus [solute] are given in Table 1 and as an example, the plot of k_{obs} against the concentration of coumarin is shown in the inset of Fig. 1. The fit of the rate data is satisfactory with an accuracy of ±5% in the measured rate constant values.

The values of the second-order rate constant measured for the reaction of the $^{\bullet}OH$ radical with coumarin and its derivatives are on average 6.2×10^9 $dm^3\,mol^{-1}\,s^{-1}$. This value is slightly lower than that reported earlier [33] ($k = 8.2 \times 10^9$ $dm^3\,mol^{-1}\,s^{-1}$) measured by the competition kinetics method under steady-state conditions. The rate constants have not shown any appreciable change due to the introduction of the substituent OCH_3 or OH group. Since the rates are diffusion-controlled, the rate constants are not expected to be influenced by the substituents. For example, this is evident from the comparison of the rate constants

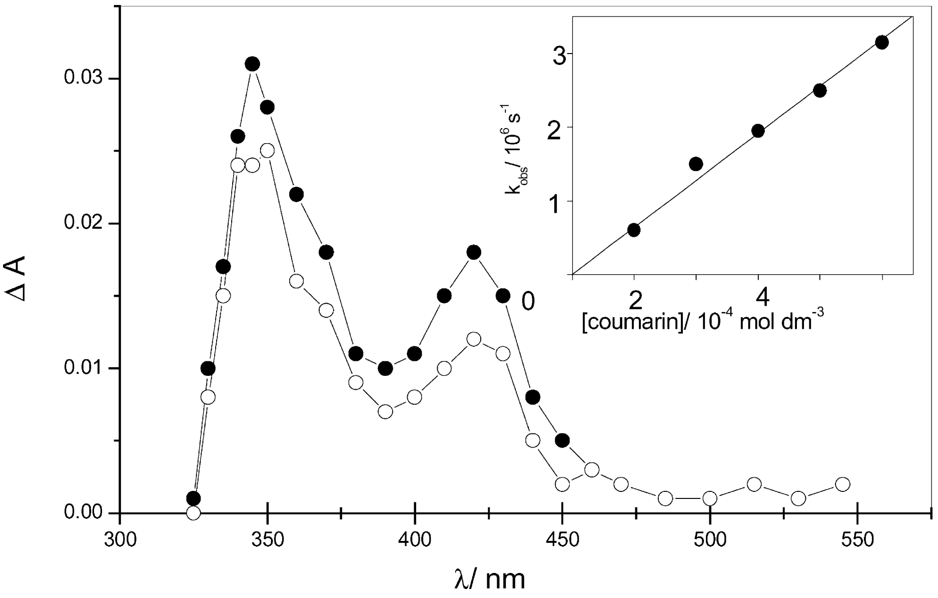


Fig. 1. The transient absorption spectra obtained for the reaction of the $^{\bullet}OH$ radical with coumarin recorded at 2 μs (●) and 40 μs (○) after the pulse. Inset: the plot of the k_{obs} versus [coumarin]. Dose per pulse = 5 Gy.

values [16] of anisole ($k = 5.4 \times 10^9$ dm^3 mol^{-1} s^{-1}), phenol ($k = 6.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) with benzene ($k = 7.8 \times 10^9$ dm^3 mol^{-1} s^{-1}).

The second rate constants measured for the $O^{\bullet -}$ reaction with coumarin and its derivatives were found to be slower ($k = (0.5–1.7) \times 10^9$ dm^3 mol^{-1} s^{-1}) as compared to those for the $^{\bullet}$OH reaction ($k \sim 6.2 \times 10^9$ dm^3 mol^{-1} s^{-1}). This diminished reactivity is attributed to the decreased electrophilicity of the reacting radical and the increased electrostatic repulsion between a negatively charged radical and the electron rich aromatic ring. Such lowering of the rate constants in the $O^{\bullet -}$ reaction was reported by us earlier in the case of other aromatic [18–23] and heterocyclic compounds [37]. The fact that the rate constant for the reaction of $O^{\bullet -}$ with 4-methyl-7-hydroxycoumarin is lower by a factor of three than that observed with 7-methoxycoumarin must be due to the difference in the reaction pathways. The $O^{\bullet -}$ radical ion is likely to abstract the H atom from the methyl group whereas it reacts via addition with 7-methoxycoumarin.

3.1.2. Reactions of $N_3^{\bullet}$ and $SO_4^{\bullet -}$

The $N_3^{\bullet}$ radical was found to be unreactive with coumarin (5×10^{-4} dm^3 mol^{-1}) and its derivatives on the pulse scale (50 μs) implying that the second-order rate constant of the reaction $\leq 10^7$ dm^3 mol^{-1} s^{-1} at the dose rate 15 Gy/pulse employed in our experiments. This observation is in accord with the reported [38] rate constants of $N_3^{\bullet}$ with benzene and derivatives ($k_{\text{benzene}} < 3 \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{\text{anisole}} < 3 \times 10^7$ dm^3 mol^{-1} s^{-1}).

The second-order rate constants obtained for the reaction of $SO_4^{\bullet -}$ with coumarin, 7-methoxycoumarin, 6,7-dimethoxycoumarin and 4-methyl-7-hydroxycoumarin in neutral solutions (pH: 7.0) are tabulated in Table 1. This value ($k \sim 5.5 \times 10^9$ dm^3 mol^{-1} s^{-1}) is comparable to that reported for anisole ($k = 4.9 \times 10^9$ dm^3 mol^{-1} s^{-1}) [39] but it is slightly higher than that measured for benzene ($k \sim 3 \times 10^9$ dm^3 mol^{-1} s^{-1}) [40]. Thus, the pyranone ring may have an activating effect on the benzene ring. Similar to the $^{\bullet}$OH radical, the rate constant values are more or less independent of the substituent.

3.1.3. Reaction of e_{aq}^-

The rate constants for the e_{aq}^- reaction with coumarin, 7-methoxycoumarin, 6,7-dimethoxycoumarin and 4-methyl-7-hydroxycoumarin by pulse radiolysis were determined from the decay of absorption at 720 nm or the transient absorption maxima at 360–380 nm. The rate determined from both these measurements are identical as is evident in the case of coumarin ($k_{\text{decay}} = 1.7 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $k_{\text{formation}} = 1.6 \times 10^{10}$ dm^3 mol^{-1} s^{-1}). Furthermore, this value is in fair agreement with that reported earlier [34] ($k = 1.6 \times 10^{10}$ dm^3 mol^{-1} s^{-1}). The rate constants obtained from k_{obs} versus [solute] with coumarin and its derivatives are diffusion-controlled with $k = (1–2) \times 10^{10}$ dm^3 mol^{-1} s^{-1} (Table 1). Because of the high reactivity, the rates do not seem to be affected by the substituents.

3.2. Transient absorption spectra

3.2.1. Reaction of $^{\bullet}$OH

The transient absorption spectra observed in the reaction of the $^{\bullet}$OH radical with coumarin in neutral solutions (pH: 6.8) was measured in the wavelength range 300–550 nm. The spectrum exhibited two peaks at 345 and 425 nm (Fig. 1) and did not show any significant time resolved changes except the normal radical–radical bimolecular decay as can be seen from the spectra recorded at 40 μs after the pulse (Fig. 1). The transient absorption spectrum with

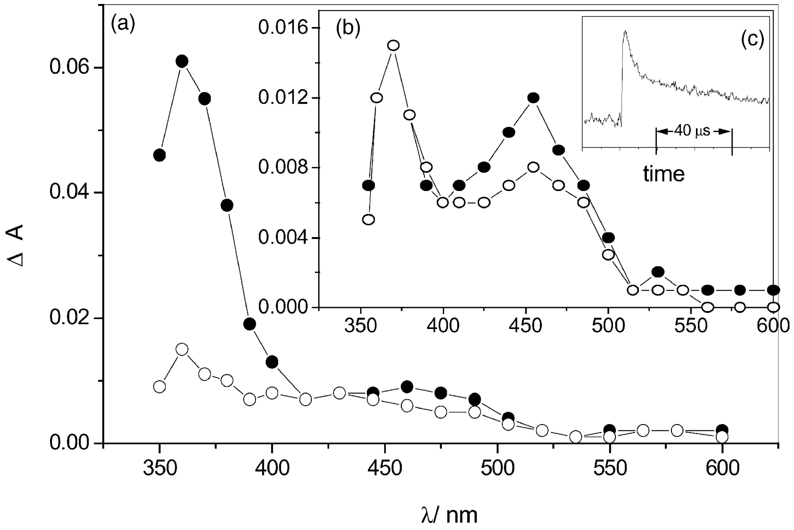


Fig. 2. The transient absorption spectra obtained for the reaction of the $^{\bullet}$OH radical with (a) 4-methyl-7-hydroxycoumarin and (b) 7-methoxycoumarin recorded at 2 μs (●) and 40 μs (○) after the pulse. (c) The decay trace at 365 nm obtained in the pulse radiolysis of 0.5×10^{-3} mol dm^{-3} N_2O saturated aqueous solution of 4-methyl-7-hydroxycoumarin.

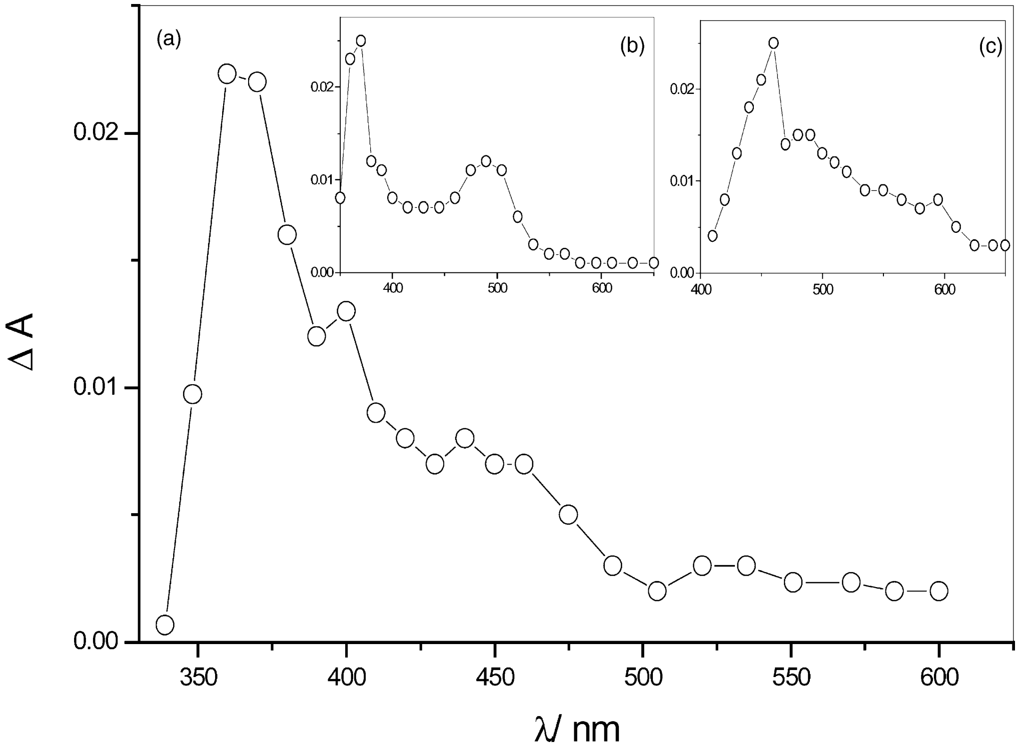


Fig. 3. The transient absorption spectra obtained for the reaction of the $O^{\bullet -}$ radical with (a) coumarin, (b) 7-methoxycoumarin and (c) 4-methyl-7-hydroxycoumarin recorded at 40 μs (○) after the pulse.

4-methyl-7-hydroxycoumarin, shown in Fig. 2a, has only one peak at 360 nm. This spectrum decayed almost completely within 40 μs after the pulse with a rate equal to $1.2\times10^{5}\,s^{-1}$. The trace corresponding to this decay is shown in Fig. 2c. The time resolved absorption spectra obtained for the reaction of the $^{\bullet}OH$ radical with 7-methoxycoumarin (Fig. 2b) is similar to that obtained with coumarin while that with 6,7-dimethoxycoumarin has a single peak at 310 nm.

The spectra observed for the reaction of the $O^{\bullet -}$ radical (pH: 13.0) with coumarin has also two peaks with maxima at 370 and 445 nm (Fig. 3a). The transient absorption spectrum for 7-methoxycoumarin ($\lambda_{max} = 365$ and 490 nm) has shown a red shift of the peak at the higher wavelength from 445 to 490 nm (Fig. 3b) whereas in the case of 4-methyl-7-hydroxycoumarin a red shift was seen in both the peaks (Fig. 3c).

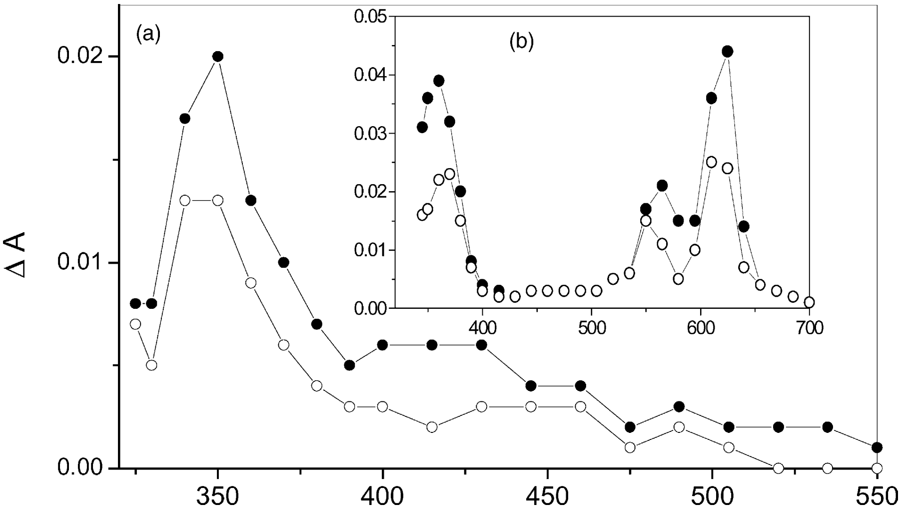


Fig. 4. The transient absorption spectra obtained for the reaction of the $SO_4^{\bullet -}$ radical with (a) coumarin, (b) 7-methoxycoumarin recorded at 2 μs (●) and 40 μs (○) after the pulse.

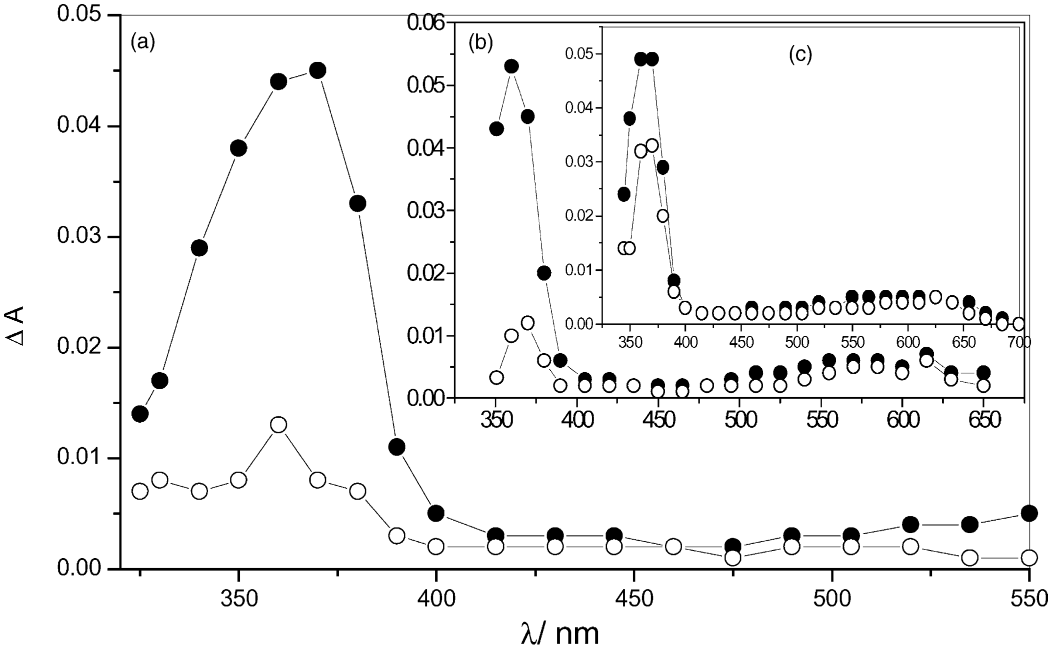


Fig. 5. The transient absorption spectra obtained for the reaction of e_{aq}^- with (a) coumarin, (b) 4-methyl-7-hydroxycoumarin and (c) 7-methoxycoumarin recorded at 2 μs (●) and 40 μs (○) after the pulse.

3.2.2. *Reaction of $SO_4^{\bullet -}$*

The transient absorption spectra from the reaction of $SO_4^{\bullet -}$ radical with coumarin at pH 7.0 exhibited a peak at 350 nm and a broad shoulder around 420 nm (Fig. 4a). This is identical to the corresponding spectrum obtained for the $^{\bullet}OH$ reaction. In the case of 4-methyl-7-hydroxycoumarin two peaks (360 and 580 nm) were seen whereas the spectra obtained with mono- and dimethoxycoumarin have three peaks at 365, 585 and 625 nm (Fig. 4b). The additional peaks in the latter indicate that the reaction pathways in the two systems are different.

3.2.3. *Reaction of e_{aq}^-*

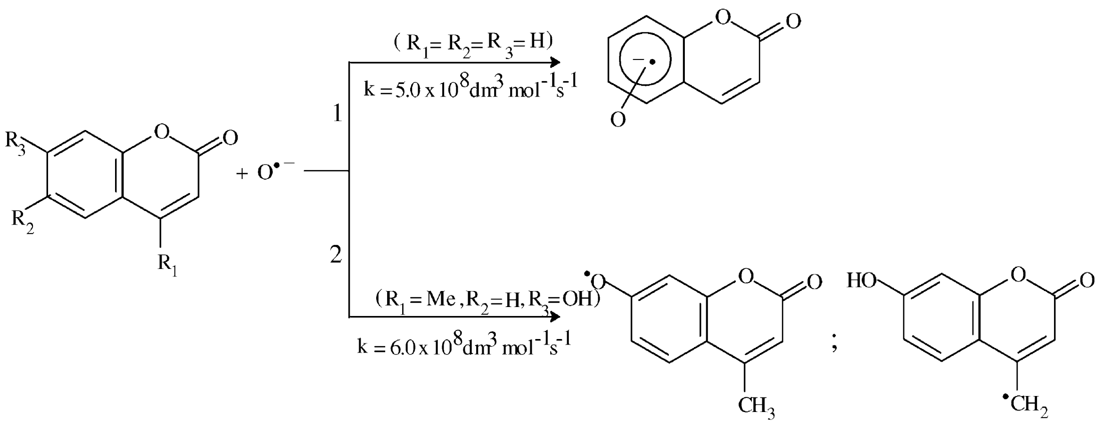
The transient absorption spectra measured for the reaction of the hydrated electron with coumarin in neutral solution (pH: 7.0) at 2 and 40 μs after the pulse, shown in Fig. 5a, has a broad peak at 350 nm which underwent considerable decay within 40 μs. The spectrum with 4-methyl-7-hydroxycoumarin has a single peak at 365 nm (Fig. 5b) which is similar to that obtained for 7-methoxycoumarin (λ_{max} = 380 nm, Fig. 5c) and 6,7-dimethoxycoumarin (λ_{max} = 385 nm). Similar to coumarin, the spectra were also observed to undergo a fast first-order decay with k values ranging from 1.1×10^4 to $4.9 \times 10^4\ s^{-1}$ and the measured rate constants are given in Table 1.

4. Reaction mechanism

The $^{\bullet}OH$ radical reacts with coumarin by addition to the electron rich aromatic ring at several sites available for attack, and thus, its addition to the relatively electron deficient pyranone ring can be ruled out. Considering, for example, coumarin and its C-6 position for the site of attack, the reaction sequence is shown in Scheme 1 (reaction (1)).

The rate constants for the bimolecular decay of the two absorption maxima of the spectrum measured in the case of coumarin were found to be nearly equal (3.0×10^9 and $2.6 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$) confirming that the spectrum is composed of a single intermediate. Thus, the observed transient absorption spectrum with the λ_{max} at 345 and 425 nm is ascribed to the equilibrium mixture of different isomeric $^{\bullet}OH$ adducts. The methoxy derivatives also react via the same mechanism to give the corresponding $^{\bullet}OH$ adducts (λ_{max} = 370, 460 nm). However, in the case of 4-methyl-7-hydroxycoumarin, the initially formed $^{\bullet}OH$ adduct loses water to give the phenoxyl radical with absorption maximum at 365 nm (reaction (2), Scheme 1) as is evident from the first-order fast decay of the spectrum. Similar fast dehydration reaction leading to the formation of phenoxyl radical has been reported earlier by us in the case of 4-hydroxybenzaldehyde [41] and 4-aminophenol [42]. No significant decay of the absorption, however, due to methanol elimination was seen in the case of the methoxy derivatives of coumarin on the time scale of 50 μs.

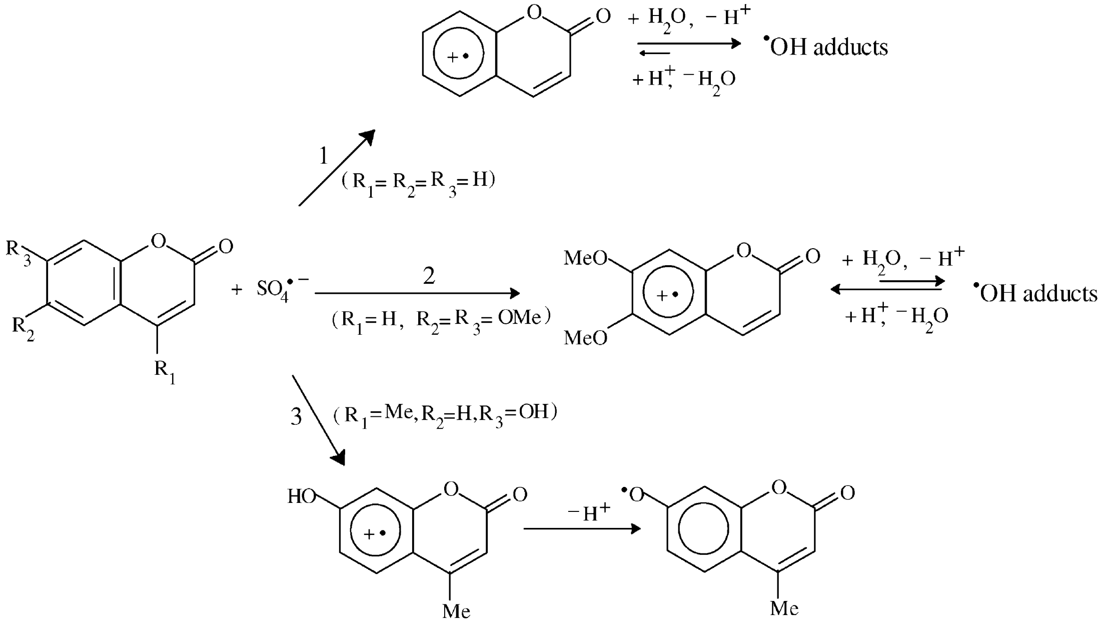
The $O^{\bullet -}$ radical is likely to react by addition to the aromatic ring (reaction (1), Scheme 2) except in the case of 4-methyl-7-hydroxycoumarin, where the hydrogen abstraction from the hydroxyl or the methyl to form a phenoxyl or a benzylic radical is a distinct possibility (reaction (2), Scheme 2).



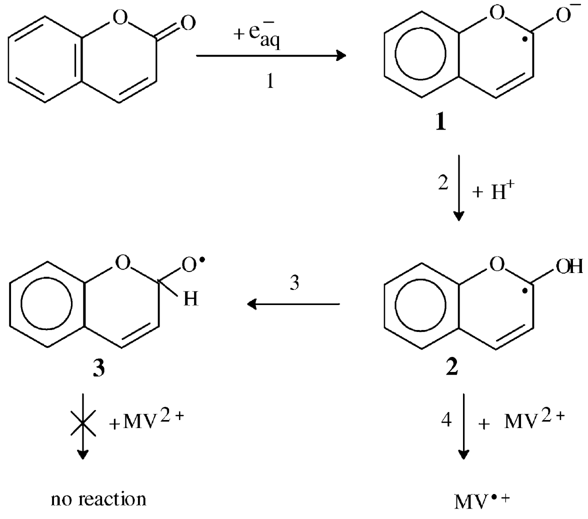
Scheme 2. Proposed mechanism of the reaction of the $O^{\bullet -}$ radical with coumarin.

The $SO_4^{\bullet -}$ radical reaction can proceed by an inner-sphere (addition/elimination) or by an outer-sphere (electron transfer) processes. The former process involves the formation of $SO_4^{\bullet -}$ adducts while the latter leads to the formation of the radical cation intermediate. The proposed mechanism of the reaction of $SO_4^{\bullet -}$ radical with coumarin and its derivatives is given in Scheme 3. The formation of the $^{\bullet}OH$ adducts occurs via the hydration of the radical cation (reaction (1)) in the case of coumarin. However, when the substrate has a methoxy group, the resultant radical cation is stabilised (reaction (2)). This is evident from the observed difference in the transient spectra obtained with coumarin ($\lambda_{max} = 350$ nm) and methoxy coumarins ($\lambda_{max} = 365$ and 585 nm). In the case of 4-methyl-7-hydroxycoumarin, the radical cation undergoes deprotonation to yield a phenoxyl radical (reaction (3)) which is supported by the observed spectrum with $\lambda_{max} = 360$ and 580 nm.

The hydrated electron reacts by adding to the carbonyl group to give initially the radical anion (reaction (1), Scheme 4) which then gets protonated to yield a neutral adduct radical (reaction (2)) similar to the fast protonation process ($k \geq 10^7\ s^{-1}$) reported [43,44] in the case of purine bases. The hetero atom protonated carbon centred electron adducts of purines was observed to undergo tautomerisation to carbon protonated hetero atom centred radical. The rate constants for this spontaneous tautomerisation reaction in neutral solutions was reported to be $k = 1 \times 10^4\ s^{-1}$ for adenine [28] and $k = 1.2 \times 10^6\ s^{-1}$ for guanosine [29]. The tautomerisation mechanism in the case adenine was reported to involve deprotonation/reprotonation processes with pK_a value of 12.1 leading finally to the formation of thermodynamically more stable carbon protonated hetero atom centred radical. However, such pK_a type of behaviour was not seen in the case of guanosine [29].



Scheme 3. Proposed mechanism of the reaction of $SO_4^{\bullet -}$ and its derivatives.



Scheme 4. Proposed mechanism of the reaction of the hydrated electron with coumarin.

The observed decay at 360 nm in the case of electron adducts of coumarin was attributed to such tautomerisation reaction with $k = 2.7 \times 10^4\,s^{-1}$ (reaction (3), Scheme 4)). Similar to the case of guanosine, no pK_a type of behaviour was observed in our study.

In order to gain further insight into the nature of the reaction intermediates, the reaction of the hydrated electron with coumarin was studied with a weak oxidant, methyl viologen (MV^{2+}), $E^\circ = -0.448$ V [17]. The rate for the oxidation of the transient species was determined by monitoring the absorption of $MV^{\bullet +}$ at 605 nm ($\varepsilon = 12{,}800\,dm^3\,mol^{-1}\,cm^{-1}$). The redox experiments were done by varying [MV^{2+}] in the range $(0.6–1.4) \times 10^{-5}\,mol\,dm^{-3}$ with the solution of $1 \times 10^{-3}\,mol\,dm^{-3}$ coumarin saturated with N_2O. Under these solution conditions, the two competing reactions are the transformation reaction (reaction (3), Scheme 4) of the hetero atom protonated electron adduct (radical 2, Scheme 4) to carbon protonated radical (radical 3, Scheme 4) and the reaction of the protonated electron adduct with MV^{2+} (reaction (4), Scheme 4) resulting in the formation of $MV^{\bullet +}$. The rate constants for the latter reaction was determined to be $1.6 \times 10^{10}\,dm^3\,mol^{-1}\,s^{-1}$. The experimentally measured $G(MV^{\bullet +})$ along with the calculated values based on the two competing reactions are given in Table 2. It can be seen that the agreement between the two values is satisfactory. In the absence of the competing tautomerisation (reaction (3), Scheme 4), the $G(MV^{\bullet +})$ was found to be 2.7. This result is consistent with the proposed reaction mechanism shown in Scheme 4.

Table 2
Experimental and calculated yields of $MV^{\bullet +}$ ($10^{-7}\,mol\,J^{-1}$) obtained in the reactions of the hydrated electron with coumarin ($1 \times 10^{-3}\,mol\,dm^{-3}$)

[MV^{2+}] (10^{-6} M)	Yields	
	Calculated	Observed
5.5	2.0	1.8
6.6	2.1	2.2
9.9	2.3	2.4
14.1	2.5	2.8

5. Conclusions

The $^\bullet$OH, e^-_{aq} and $SO_4^{\bullet -}$ react with coumarin and its derivatives at diffusion-controlled rates with $k > 10^9\,dm^3\,mol^{-1}\,s^{-1}$. The rates of the $^\bullet$OH and $SO_4^{\bullet -}$ radical with coumarin and its derivatives do not differ appreciably with the introduction of various substituents OH or OCH_3. The transient absorption spectra in the $^\bullet$OH reaction with these coumarins are assigned to the $^\bullet$OH adduct radicals. In the case of 4-methyl-7-hydroxycoumarin, the initially formed $^\bullet$OH adduct undergoes dehydration to give phenoxyl radical. The $SO_4^{\bullet -}$ reaction with coumarin leads to the formation of the radical cation which is stabilised by the electron donating methoxy groups or deprotonated generating the phenoxyl radical in 4-methyl-7-hydroxycoumarin. The hydrated electron reaction mechanism is similar to that observed in the case of purine bases.

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