

Pulse Radiolytic Investigations of Hydroxy-radical Reactivities in Micellar Solutions

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Summary Rate constants for reactions of $\text{OH}\cdot$ with charged and neutral surfactants are substantially smaller above the critical micelle concentrations than below them; rate constants for $\text{OH}\cdot$ addition to C_6H_6 are also smaller in micellar systems than in water.

THE rates of numerous organic reactions are enhanced or retarded significantly in the presence of neutral and charged association colloids or micelles.¹ These effects are the result of electrostatic, hydrophobic and other specific interactions which lower or raise the overall free energy requirement of the given reaction. Owing to the importance of hydroxy-radical reactions, we report here a marked

difference in the rate constants for the $\text{OH}\cdot$ reactions, with different surfactants, below and above the critical micelle concentration, as well as substantial micelle effects on the addition of $\text{OH}\cdot$ to benzene.

The reactivity of $\text{OH}\cdot$ towards anionic sodium dodecyl sulphate (NaLS), $\text{Me}(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$, and nonionic polyoxyethylene(15) nonylphenol (Igepal CO-730), $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{14}\text{CH}_2\text{CH}_2\text{OH}$, was determined pulse radiolytically using the thiocyanate competition method.² The reaction was followed optically by the measurement of the absorbance of the intermediate $(\text{CNS})_2^-$ at 500 nm. The value of $k(\text{OH}\cdot + \text{CNS}^-)$ was taken to be $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.³ The Figure shows the thiocyanate competition plots for NaLS and Igepal CO-730. The critical micelle concentration for NaLS is reported to be 8×10^{-3} while that of Igepal CO-730 is 1×10^{-4} .⁴ The marked breaks in these plots at concentrations which coincide with the critical micelle concentration region of these surfactants indicate that the rate constants for the $(\text{OH}\cdot + \text{surfactant})$ reaction are smaller above the critical micelle concentration than below it. The calculated rate constants for these surfactants are presented in the Table. Since these are independent of KCNS concentrations, the possibility of differential $\text{OH}\cdot$ scavenging by the CNS^- ion in micellar solutions is unlikely.

Rates for the reaction of cationic hexadecyltrimethylammonium bromide (CTAB) with $\text{OH}\cdot$ were measured at surfactant concentrations above and below the critical micelle concentration ($9 \times 10^{-4} \text{ M}$)¹ and are also given in the Table. In each case the concentration of MeOH as a competitive $\text{OH}\cdot$ scavenger was varied and the decrease in the yield of Br_2^- optically monitored at 360 nm. The value of $8.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was taken for $k(\text{OH}\cdot + \text{MeOH})$.^{5†} The marked difference in the reactivity of $\text{OH}\cdot$ radicals towards surfactants above and below their critical micelle concentrations brings into question the validity of extending rate constant determinations of $\text{OH}\cdot$ reactions from aqueous

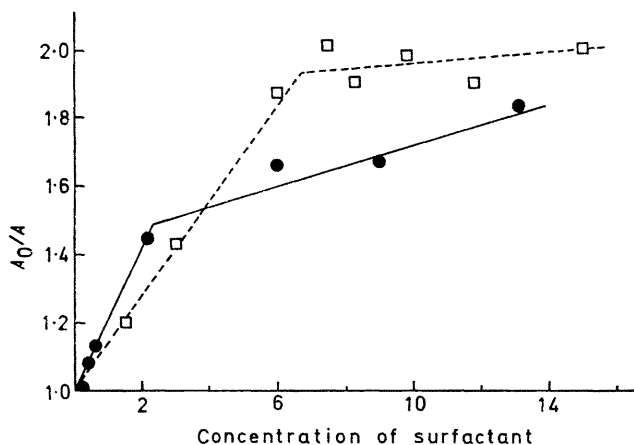


FIGURE. Plot of absorbance ratios (A_0/A) versus surfactant concentration in KCNS competition studies: ---- NaLS in $5 \times 10^{-3} \text{ M}$ -KCNS, the concentration scale represents $[\text{NaLS}] \times 10^3 \text{ M}$; — Igepal CO-730 in $5 \times 10^{-4} \text{ M}$ -KCNS, the concentration scale represents $[\text{Igepal}] \times 10^4 \text{ M}$. A_0 and A are the $(\text{CNS})_2^-$ absorbances in the absence and presence of surfactant, respectively.

† The value of $k(\text{OH}\cdot + \text{MeOH})$ taken from competition measurements (cf. ref. 5) has been updated in terms of the more recent value of $k(\text{OH}\cdot + \text{CNS}^-)$ (cf. ref. 3).

solutions to biological macromolecules which exist, in many cases, as heterogeneous aggregates.

Igepal CO-730,^{1,8} The rate retardation by the anionic and neutral micelles is therefore likely to be the result of the

Rate constants for OH· reactions with surfactants and with C₆H₆ in the presence of surfactants (sft)

Surfactants	$k(\text{OH}\cdot + \text{sft})$ (l mol ⁻¹ s ⁻¹) C _{sft} < CMC ^a	$k(\text{OH}\cdot + \text{sft})$ (l mol ⁻¹ s ⁻¹) C _{sft} > CMC	$k(\text{OH}\cdot + \text{C}_6\text{H}_6)^{\text{b}}$ (l mol ⁻¹ s ⁻¹) C _{sft} > CMC
NaLS	7.6 × 10 ⁹	0.5 × 10 ⁹	3.0 × 10 ⁹
Igepal (CO-730)	1.1 × 10 ¹⁰	1.7 × 10 ⁹	2.6 × 10 ⁹
CTAB	1.04 × 10 ¹⁰	2.1 × 10 ⁹	2.6 × 10 ⁹
None	—	—	8.2 × 10 ^{9c}

^a CMC = critical micelle concentration. ^b The surfactant concentration in each case except NaLS exceeded the CMC by not less than a factor of five. ^c This is the rate constant for (benzene + OH·) in the aqueous phase.

Rate constants for the reaction of OH· with C₆H₆ in the presence of these surfactants have also been determined by extending the competition technique to a three component system (surfactant-C₆H₆-competitor) and are included in the Table. The value of $k(\text{OH}\cdot + \text{C}_6\text{H}_6)$ in the aqueous phase (Table), was determined from CNS⁻ competition. Good agreement exists between this and the value recently reported by Michael and Hart [$k(\text{OH}\cdot + \text{C}_6\text{H}_6) = (7.6 \pm 1.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$].⁶ In all three surfactants, rates in the micellar phase are substantially smaller than those in the aqueous bulk phase. From n.m.r. determinations it is known that C₆H₆ is solubilized by all three detergents. These studies indicate that C₆H₆ lies near the micelle-water interface in the case of CTAB, while located in the hydrocarbon core of NaLS⁷ and such neutral micellar species as

substrate being less accessible to OH· inside the micelle than in the bulk phase. The finding that the rate constant for (e_{aq}⁻ + C₆H₆) is enhanced⁹ ($k^{\text{CTAB}}/k^{\text{H}_2\text{O}}$ ca. 7) but that for (OH· + C₆H₆) is retarded by micellar CTAB emphasizes the difference in polarity of e_{aq}⁻ and OH·. Electrostatic interaction between the π-electron system of the C₆H₆ molecule and the net positive charge on the micellar CTAB surface would render benzene more susceptible to nucleophilic attack by the electrons.⁹ OH· on the other hand, is considered to have electrophilic properties,¹⁰ and its approach to the solubilized benzene is therefore hindered electrostatically by the positively charged CTAB micelle.

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