Steady State and Pulse Radiolysis Studies of $Cl_2^{-\cdot}$ Reactivity in Micellar Systems

By J. H. FENDLER,* E. J. FENDLER, and G. BOGAN
(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

and L. K. PATTERSON and K. M. BANSAL
(*Radiation Research Laboratories, Mellon Institute of Science, Pittsburgh, Pa.*, 15213)

Summary Rate constants for reactions of $Cl_2^{-\cdot}$ with charged and neutral surfactants are significantly smaller above the critical micelle concentrations than below them; the subsequent reactions, rather than the formation of the uracil–$Cl_2^{-\cdot}$ adduct, are affected by micellization.

CHROMOPHORIC groups present in pyrimidines, nucleosides, and nucleotides are known to be selectively sensitized or protected from radiation effects by the presence of chloride ions in acidic aqueous solutions.[1–3] In these solutions hydroxyl radicals are rapidly converted into $Cl_2^{-\cdot}$ (reactions

1 and 2) which interacts with pyrimidine bases.[4] The

$$\cdot\mathrm{OH} + \mathrm{Cl}^- \longrightarrow \cdot\mathrm{Cl} \tag{1}$$

$$\cdot\mathrm{Cl} + \mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2^{\bar{\cdot}} \tag{2}$$

effects on chromophoric groups, however, are mainly due to differences in reactions subsequent to the formation of $\mathrm{Cl}_2^{\bar{\cdot}}$ or ·OH adducts.[2,3] Due to the importance of radiation protection and sensitization in biological systems, which in many cases contain relatively high concentrations of chloride ion, we are investigating the radiation induced reactions of $\mathrm{Cl}_2^{\bar{\cdot}}$ with uracil in the presence of charged and neutral surfactants, which provide a better approximation of the environment of biological systems than does water.[5,6] We report significant surfactant effects on the $\mathrm{Cl}_2^{\bar{\cdot}}$ sensitized chain reaction which leads to the destruction of uracil and marked differences in the reactivity of $\mathrm{Cl}_2^{\bar{\cdot}}$ both above and below the critical micelle concentration (CMC), toward the surfactants used: *cationic* hexadecyltrimethylammonium chloride (CTACl), $\mathrm{CH_3(CH_2)_{15}(CH_3)_3N^+Cl^-}$, *anionic* sodium dodecyl sulphate (NaLS), $\mathrm{CH_3(CH_2)_{11}SO_4^-Na^+}$ and *nonionic* polyoxyethylene(15)nonylphenol (Igepal CO-730), $\mathrm{C_9H_{19}C_6H_4O(CH_2CH_2O)_{14}CH_2CH_2OH}$. All irradiations were carried out in triple distilled, air saturated (to scavenge e^-_{aq} and ·H) water.

Rate constants for the initial step, the formation of the $\mathrm{Cl}_2^{\bar{\cdot}}$ adduct, with surfactants and uracil were determined pulse radiolytically by monitoring the disappearance of $\mathrm{Cl}_2^{\bar{\cdot}}$ absorption at 360 nm. In the absence of solutes, $k(\mathrm{Cl}_2^{\bar{\cdot}} + \mathrm{Cl}_2^{\bar{\cdot}})$ was found to be $(1{\cdot}2 \pm 0{\cdot}3) \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ ($\epsilon_{360} = 10{,}000$) in good agreement with previously reported values.[1,7] Rate constants for the reaction of $\mathrm{Cl}_2^{\bar{\cdot}}$ with surfactants were measured, where possible, above and below the CMC (see Table). The corresponding values for hydroxyl radical reactivities with Igepal CO-730 and NaLS are also given for purpose of comparison. Rates for the interaction of uracil with $\mathrm{Cl}_2^{\bar{\cdot}}$ were measured in both the presence and the absence of surfactants. In CTACl systems above the CMC pulse radiolytic measurement was not possible due to complications arising from a transient related to the surfactant itself.

Surfactant effects on the overall chain destruction of uracil induced by $\mathrm{Cl}_2^{\bar{\cdot}}$ in steady state irradiation studies were measured by competition methods. G(-Uracil) as a function of increasing surfactant concentration was calculated from changes in the absorption of uracil 250 nm. The irradiations were carried out in a cobalt-60 γ-ray source at an absorbed dose rate of $1{\cdot}25 \times 10^{14}\ \mathrm{eV\ g^{-1}\ min^{-1}}$. Plots of 1/G(-uracil) *vs.* [surf]/[uracil] where surf = surfactant were constructed from which the ratios of $k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})/k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$ were calculated. These ratios, taken above and below the CMC as well as values of $k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})$ obtained from competition measurements based on $k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}}) = 3{\cdot}5 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ are given in the Table. This latter value is in good agreement with that previously reported.[1] Measurements taken above the CMC, where [surf] represents the surfactant in micellar form, were corrected for monomer surfactant reactivity assuming a constant monomer concentration equal to the CMC.

The Table indicates that in each surfactant system, the formation of micelles markedly reduces the surfactant reactivity toward $\mathrm{Cl}_2^{\bar{\cdot}}$. This behaviour parallels that of ·OH toward surfactants,[8] in which case NaLS is more affected by micelle formation than Igepal CO-730. However, the values of $k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})$ are *ca.* 2 orders of magnitude lower than those of $k(\mathrm{surf} + \cdot\mathrm{OH})$. In several organic systems the $\mathrm{Cl}_2^{\bar{\cdot}}$ reaction rate constants are found to be 20—200 times less than the values for the corresponding hydroxyl radical reactions.[1,7] The ratios of $k(\mathrm{monomer} + \mathrm{Cl}_2^{\bar{\cdot}})/k(\mathrm{micelle} + \mathrm{Cl}_2^{\bar{\cdot}})$ are much higher than $k(\mathrm{monomer} + \cdot\mathrm{OH})/k(\mathrm{micelle} + \cdot\mathrm{OH})$ as indicated in the Table. This suggests a greater inability of $\mathrm{Cl}_2^{\bar{\cdot}}$ to penetrate the outer micelle layer to reactive sites, especially in the case of *anionic* NaLS where some anion–anion repulsion arising from the negatively charged micelle surface could occur. The pulse radiolysis data for $k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$ indicate that only in the presence of Igepal CO-730 is there any micellar effect in evidence, $k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$ being constant in the presence of other surfactants. However, in the Igepal CO-730 system, the difference in $k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})$ obtained from pulse and steady state studies are too large to be explained by the alteration in $k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$ observed in the pulse experiments. This large disparity indicates that both monomeric and micellar Igepal CO-730 interfere in the chain mechanism of uracil destruction at other than the initial $\mathrm{Cl}_2^{\bar{\cdot}}$–uracil interaction to which the

Rate constants for the reaction of $\mathrm{Cl_2^-}$ *with surfactants and with uracil in the presence of surfactants* (k *is given in units of* $\mathrm{M^{-1}\ s^{-1}}$)[a]

	$k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})/k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$		$k(\mathrm{surf} + \mathrm{Cl}_2^{\bar{\cdot}})$		$k(\mathrm{uracil} + \mathrm{Cl}_2^{\bar{\cdot}})$		$k(\mathrm{surf} + \cdot\mathrm{OH})$[h]	
Surfactant	C_{surf} < CMC	C_{surf} > CMC	C_{surf} < CMC	C_{surf} > CMC	C_{surf} < CMC	C_{surf} > CMC	C_{surf} < CMC	C_{surf} > CMC
Igepal CO-730								
Pulse radiolysis[b]			$2{\cdot}3\times10^8$	$2{\cdot}8\times10^7$	$3{\cdot}5\times10^7$	*ca.* 1×10^8	$1{\cdot}1\times10^{10}$	$1{\cdot}7\times10^9$
Competition[b]	68·2	10·3[c]	$2{\cdot}4\times10^9$	$3{\cdot}6\times10^8$				
CTACl								
Pulse radiolysis[d]			$1{\cdot}2\times10^7$		$3{\cdot}5\times10^7$			
Competition[d]	$2{\cdot}47\times10^{-1}$	$3{\cdot}84\times10^{-2}$	$8{\cdot}6\times10^6$	$1{\cdot}3\times10^6$				
NaLS[d]								
Pulse radiolysis[e]					$3{\cdot}5\times10^7$	$3{\cdot}5\times10^7$	$7{\cdot}6\times10^9$	$5{\cdot}0\times10^8$
Competition[f]	$7{\cdot}52\times10^{-2}$	$6{\cdot}9\times10^{-4}$	$2{\cdot}6\times10^6$	$2{\cdot}4\times10^4$				
None					$3{\cdot}5\times10^7$[g]			

[a] C_{surf} > CMC indicates that the critical micelle concentration is exceeded by at least a factor of five; [b] solutions contained 0·10 M NaCl at pH ~ 2·0 ($\mathrm{HClO_4}$); CMC = $9{\cdot}7 \times 10^{-5}$ M; [c] solutions contained 0·1 M NaCl at pH = 1 ($\mathrm{HClO_4}$); [d] solutions contained 0·1 M HCl; CMC = $1{\cdot}3 \times 10^{-3}$ M; [e] solutions contained 0·1 M NaCl at pH = 2·0 ($\mathrm{HClO_4}$); CMC = $1{\cdot}4 \times 10^{-3}$ M; [f] solutions contained 0·5 M NaCl at pH = 2 ($\mathrm{HClO_4}$); [g] rate constant for uracil + $\mathrm{Cl}_2^{\bar{\cdot}}$ determined pulse radiolytically in water; [h] reference 8.

pulse experiments are responsive. Conversely, in the monomeric CTACl system where pulse radiolysis measurements were possible, the good agreement between pulse radiolysis and steady state values indicates no significant interference by the surfactant either at the initial or any subsequent step in the chain mechanism.

In NaLS systems no pulse radiolysis measurements of $k(\text{surf} + \mathrm{Cl}_2^{-\cdot})$ were possible owing to the very low apparent reactivity of $\mathrm{Cl}_2^{-\cdot}$ toward both monomeric and micellar forms. Due to the nature of competition studies, the values of $k(\text{surf} + \mathrm{Cl}_2\cdot)$ for NaLS must be considered to be upper limits. The wide variation of $k(\text{surf} + \mathrm{Cl}_2^{-\cdot})$ for the systems under study illustrates again the sensitivity of reactivity of charged species to surfactant structure.

Studies of micellar effects on related reactions involving other pyrimidines and nucleic acid constituents are in progress.

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