Micellar Effects on $Cl_2^{\bullet -}$ Reactivity. Reactions with Surfactants and Pyrimidines[1]

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Abstract: Reactivities of $Cl_2 \cdot^-$ with micelle-forming surfactants and with uracil, 5-chlorouracil, thymine, cytosine, and cytidine both in aqueous and micellar systems have been investigated. Rate constants for initial reactions of $Cl_2 \cdot^-$ with surfactants and with these pyrimidines have been measured by pulse radiolysis where possible. Steady-state studies of competition between pyrimidines and surfactants for $Cl_2 \cdot^-$ were carried out by determination of $G(-\text{pyrimidine})$ following Co-60 γ-cell irradiation. It has been shown by combining data from these two methods that $k_{Cl_2 \cdot^- + \text{surfactant}}$ is smaller above the critical micelle concentration than below it. Although little or no micellar effect is observed on the initial reaction between $Cl_2 \cdot^-$ and uracil or its derivatives (thymine and 5-chlorouracil), it is evident that there is interference which in subsequent processes lowers $G(-\text{pyrimidine})$. In cytosine and cytidine systems some initial effects are evident at concentrations of these compounds of about 5×10^{-3} *M*. In addition, $G(-\text{cytosine})$ and $G(-\text{cytidine})$, in the presence of micellar hexadecyltrimethylammonium chloride, are greater than in the presence of monomeric surfactant.

The presence of chloride ions in irradiated acidic air-saturated aqueous solutions has been shown to increase the base destruction yields of uracil and cytosine, to have no effect on those for thymine, and to decrease those for nucleotides and nucleosides.[4-7] γ irradiation of aqueous air-saturated acidic sodium chloride solutions results in the following processes.[8,9]

$$H_2O \xrightarrow{\sim\sim} e_{aq}^- + \cdot H + \cdot OH + H_2 + H_2O_2 \quad (1)$$

$$e_{aq}^- + H_3O^+ \longrightarrow \cdot H + H_2O \quad (2)$$

$$\cdot H + O_2 \longrightarrow H\dot{O}_2 \quad (3)$$

$$\dot{O}H + Cl^- + H_3O^+ \longrightarrow Cl\cdot + 2H_2O \quad (4)$$

$$Cl\cdot + Cl^- \longrightarrow Cl_2 \cdot^- \quad (5)$$

In the presence of pyrimidines, $H\dot{O}_2$ is assumed to be unreactive.[6] It has been suggested that the $Cl_2 \cdot^-$ radical oxidizes the pyrimidine molecule

$$\text{pyrimidine} + Cl_2 \cdot^- \longrightarrow \text{pyrimidine} \cdot^+ + 2Cl^- \quad (6)$$

and that the resulting cation radical reacts subsequently with oxygen and other pyrimidine molecules. In the case of uracil, formation of polyperoxides has been suggested.[6] It is apparent that the overall radical processes differ for various nucleic acid constituents.

We have suggested that irradiation of substrates in micellar solutions provides a better approximation of the microenvironment involved in radiation biological processes than does pure water[10-12] and have found varying effects on the rate constants for primary radical–substrate reactions.[11,12] Since radiation protection and sensitization by chloride ions have important biological consequences, we have investigated the radiation-induced reactions of $Cl_2 \cdot^-$ with micelle forming surfactants, and with uracil, 5-chlorouracil, thymine, cytosine, and cytidine in the presence of surfactants. Both pulse radiolysis and steady-state techniques have been employed. The former was used to provide direct information on the initial rate processes and the latter on the overall radical reactions. Combination of these two techniques allows more detailed elucidation of the mechanisms involved in these radiation-induced reactions.

Experimental Section

Preparation and purification of the surfactants have been described.[13,14] Igepal CO-730, a gift from General Aniline and Film Corp., was used without further purification. Surface tension determinations of the critical micelle concentration (cmc) of each of the surfactants at 25.0° were carried out using a du-Nöuy tensiometer. No minima in plots of the surface tension *vs.* surfactant concentration were observed, indicating the absence of impurities. The purity of the surfactants was also confirmed by the absence of observable impurities in their ir and ^1H nmr spectra. Reagent grade uracil, 5-chlorouracil, thymine, cytosine, cytidine (Sigma), and sodium chloride (Mallinckrodt) were used without further purification. Triply distilled water was used to prepare the solutions and all of the glassware used was previously baked at 500° or above. The pulse radiolysis apparatus used has been described elsewhere;[15] these pulse radiolytic studies were carried out at pH 2.0 in the presence 0.10 *M* NaCl with the exception of CTACl containing solutions where 0.01 *M* HCl was used.

Steady-state irradiations were carried out in a ^{60}Co γ-ray source at an absorbed dose rate of 1.2×10^{14} eV g^{-1} min^{-1}. Dosimetry of the γ-ray source was determined and was checked at regular intervals by means of Fricke solutions. $G(-\text{pyrimidine})$ values were obtained from spectrophotometric determinations of the pyrimidine concentration after irradiation at the appropriate wavelength

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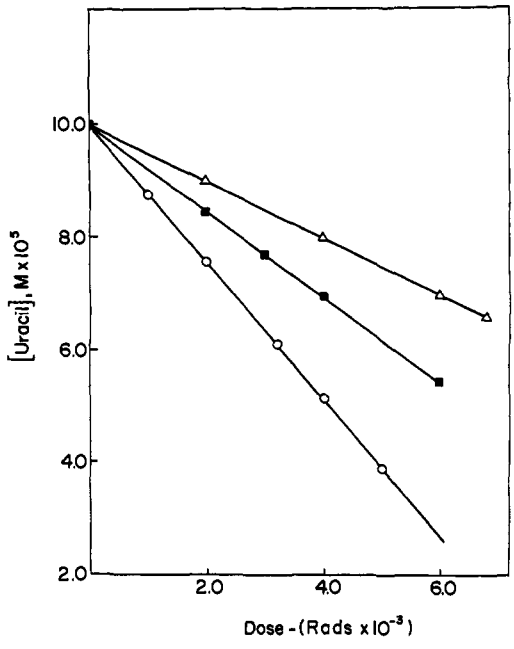

Figure 1. Change in uracil concentration as a function of absorbed dose: [uracil] = 1.0×10^{-4} *M*, [NaCl] = 5.0×10^{-1} *M*, [$HClO_4$] = 1.02×10^{-2} *M*; [NaLS] = 0 *M* (○), 5.0×10^{-4} *M* (□), 4.0×10^{-3} *M* (△).

using a Beckman DU spectrophotometer; the reference solutions were identical in composition with the exception of the pyrimidine. In all cases good linear yield–dose plots were obtained. Typical plots are illustrated in Figure 1. All measurements were carried out in air-saturated solutions.

Results and Discussion

As in previous investigations we have utilized a surfactant of each charge type for the study of micellar effects: *cationic* hexadecyltrimethylammonium chloride (CTACl); *anionic* sodium dodecyl sulfate (NaLS); and *nonionic* Igepal CO-730. Hexadecyltrimethylammonium chloride was used rather than the corresponding bromide (CTAB) in order to avoid the problem of mixed counterions in the surfactant solutions.

Pulse Radiolysis Studies of the Reactions of $Cl_2 \cdot^-$ with Pyrimidines and with Surfactants. Rate constants for the initial reactions of $Cl_2 \cdot^-$ with these surfactants and with the pyrimidines have been determined, where possible, by pulse radiolysis. All kinetic measurements were carried out by monitoring pseudo-first-order decays of the $Cl_2 \cdot^-$ transient at its absorption maximum of 340 nm as a function of scavenger concentration. A value for $2k_{Cl_2 \cdot^- + Cl_2 \cdot^-}$ was found, in 10^{-1} *M* NaCl solutions at pH 1.9, to be $1.2 \pm 0.3 \times 10^{10}$ M^{-1} sec^{-1} in good agreement with literature values.[5,16] Hence, by employing low doses of radiation, 150–200 rads, it has been possible to follow the decays related to scavenger reactions, making in subsequent calculations small corrections for contribution from $Cl_2 \cdot^- + Cl_2 \cdot^-$ interaction.

Rate constants for reactions of $Cl_2 \cdot^-$ with NaLS and Igepal CO-730 above their cmc's were obtained. Though values below the cmc were obtained in the case of Igepal CO-730, the low reactivity of NaLS prevented direct determination of $k_{Cl_2 \cdot^- + NaLS}$ for the monomeric form. In fact, the value reported for micellar NaLS represents an upper limit and probably includes an appreciable contribution from the reaction of the monomeric species. These rate constants are given in Table I. A value for monomeric CTACl was also obtained. However, in the presence of this surfactant there is a shift in the absorption maximum from 340 to 360 nm and an actual transient growth rather than decay in the region below 300 nm as a function of time. This is illustrated in Figure 2. It was, then, not possible to measure directly the rate constant above the cmc and the values for this system and that for monomeric NaLS given in Table I were taken from competition studies discussed below. The dependence of $k_{Cl_2 \cdot^- + Igepal}$ upon Igepal concentration is shown in Figure 3, illustrating the marked change in reactivity of

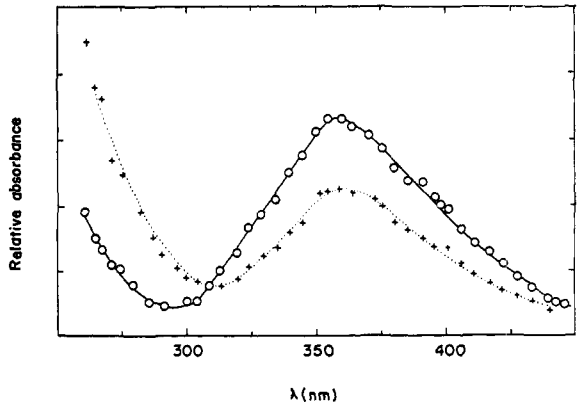

Figure 2. Transient absorption spectra from pulse radiolysis of 4×10^{-3} *M* CTACl in 0.01 *M* HCl aqueous solution: (○) immediately after the pulse, (+) 20 μsec after the pulse.

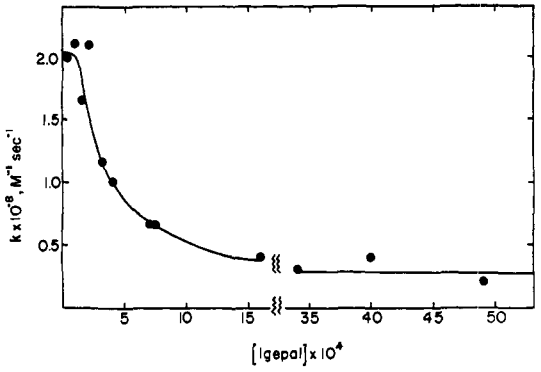

Figure 3. $k_{Igepal\ CO-730+Cl_2 \cdot^-}$ values determined pulse radiolytically as a function of surfactant concentration.

Table I. Rate Constants for the Reactions of $Cl_2 \cdot^-$ with Surfactants[a]

Surfactant	Cmc, *M*	$k_{Cl_2 \cdot^- + surf}$, M^{-1} sec^{-1} Below cmc	Above cmc
Igepal CO-730[b]	9.0×10^{-5} [c]	2.1×10^8 (1.1×10^{10})	2.8×10^7 (1.7×10^9)
CTACl	1.3×10^{-3} [d]	1.2×10^7 [e]	
NaLS	1.4×10^{-3} [f]	3.9×10^6 [e] (7.6×10^9)	$<10^4$ (5.0×10^8)

[a] Determined by pulse radiolysis, unless stated otherwise; values in parentheses are rate constants for ·OH + surfactant, obtained in ref 11. [b] See Figure 3. [c] At 25.0° in the presence of 0.10 *M* NaCl at pH 2 ($HClO_4$). [d] At 30.0° in water. [e] See Discussion. [f] At 25.0° in the presence of 0.5 *M* NaCl.

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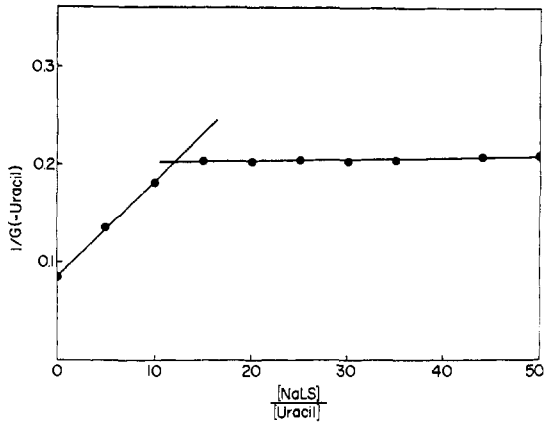

Figure 4. Competition plot for $Cl_2 \cdot^-$ reaction with uracil and with NaLS: $[HClO_4] = 1.02 \times 10^{-2}$ *M*, $[NaCl] = 5.0 \times 10^{-1}$ *M*. Concentration of NaLS above the cmc corrected for monomers.

$Cl_2 \cdot^-$ with the surfactant in the region just above the cmc. Of course the values of $k_{Cl_2 \cdot^- + Igepal}$ given reflect both reactions of monomeric and of micellar Igepal in this concentration range, resulting in a gradual rather than sharp drop in the rate constant. It may be seen that $Cl_2 \cdot^-$ is far less reactive toward both ionic surfactants than toward the neutral Igepal. This may be due to the polyethoxy groups of the latter. Also, from Table I, it is observed that a decrease in $k_{Cl_2 \cdot^- + NaLS}$ of two orders of magnitude occurs upon micelle formation, a larger change than any observed in these or similar studies.[10-12] The formation of a negatively charged surface layer through which the $Cl_2 \cdot^-$ radical anion must penetrate for reaction may account for this behavior. In general, it may be seen that these observed changes in reactivity parallel behavior observed in ·OH reactions although the absolute rate constants are generally about two orders of magnitude less when $Cl_2 \cdot^-$ is involved rather than OH·. This is not surprising since for several organic compounds $Cl_2 \cdot^-$ has been found to be 20–200-fold less reactive than ·OH.[5]

Rate constants for reactions of uracil, thymine, 5-chlorouracil, cytosine, and cytidine—each with $Cl_2 \cdot^-$—were also measured and, save for cytosine, were found to be in reasonable agreement with those values previously reported.[5] These are given in Table II. The low reactivity of NaLS allowed convenient measurement of micellar effects on these reactions. For pyrimidine concentrations of 5×10^{-3} *M*, values of $k_{Cl_2 \cdot^- + pyrimidine}$ in the presence of 0.04 *M* NaLS are also given in Table II. Though the reactions involving uracil and its derivatives, thymine and 5-chlorouracil, show little or no micellar effect (only that for 5-chlorouracil is measurable), both cytosine and its ribose nucleotide, cytidine, show markedly less reactivity toward $Cl_2 \cdot^-$ in the presence of micellar NaLS. This may indicate some solubilization of the substrate in the micellar phase whereas the first three compounds do not appear to be significantly solubilized by NaLS.

Table II. Pulse Radiolytic Rate Constants for the Reactions of $Cl_2 \cdot^-$ with Pyrimidines[a]

	$k_{Cl_2 \cdot^- + pyrimidine}$, M^{-1} sec^{-1}	
	In water	In aqueous 4.0×10^{-2} *M* NaLS
Uracil	3.5×10^7 (4.1×10^7)[b]	3.5×10^7
Thymine	7.0×10^7 (1.2×10^8)[b]	7.0×10^7
Cytosine	1.0×10^7 (9×10^7)[b]	5.0×10^6
5-Chlorouracil	1.0×10^7	5×10^6
Cytidine	4×10^6	2×10^6

[a] Each rate constant represents at least three determinations at different concentrations at pH 2.0. [b] Determined in ref 5.

Competition between Surfactants and Pyrimidines for $Cl_2 \cdot^-$ Steady-State Radiolysis. It is clear that much of the destruction initiated by $Cl_2 \cdot^-$ occurs in secondary reactions[5] whose observation is not in the range of our pulse radiolysis apparatus. To obtain information about micellar effects on these processes, steady-state competition studies utilizing low radiation dose rates were employed. The competition between the reactions

$$\text{surfactant} + Cl_2 \cdot^- \xrightarrow{k_7} P_1 \quad (7)$$

$$\text{pyrimidine} + Cl_2 \cdot^- \xrightarrow{k_8} P_2 \quad (8)$$

is described by

$$G(-\text{pyrimidine}) = G(-\text{pyrimidine})_0 \times \frac{k_8[\text{pyrimidine}]}{k_8[\text{pyrimidine}] + k_7[\text{surfactant}]} \quad (9)$$

where $G(-\text{pyrimidine})$ and $G(-\text{pyrimidine})_0$ are the base destruction yields in the presence and absence of the surfactant competitor, k_7 and k_8 are the rate constants for reactions 7 and 8, and [surfactant] and [pyrimidine] denote the stoichiometric concentrations of the competing solutes. Rearrangement of eq 9 results in eq 10. Keeping the concentration of pyrimidine con-

$$\frac{1}{G(-\text{pyrimidine})} = \frac{1}{G(-\text{pyrimidine})_0} + \frac{1}{G(-\text{pyrimidine})_0} \frac{k_7[\text{surfactant}]}{k_8[\text{pyrimidine}]} \quad (10)$$

stant while varying surfactant, a plot of $1/G(-\text{pyrimidine})$ *vs.* [surfactant]/[pyrimidine] should give a straight line with $1/G(-\text{pyrimidine})_0$ as the intercept and $[1/G(-\text{pyrimidine})_0](k_7/k_8)$ as the slope. This is true provided the $G(-\text{pyrimidine})$ for each initial interaction remains unchanged. Figure 4 illustrates such a plot for the competition between uracil and sodium dodecyl sulfate for $Cl_2 \cdot^-$. The coincidence of the break in the competition plot with the aggregation of the surfactant, *i.e.*, with the cmc (1.4×10^{-3} *M*), implies a difference between the ratios of reactivities, k_7/k_8, below and above the cmc. Analogous competition plots for a number of pairs of competitors gave similar results. Ratios of relative reactivities below and above the cmc values have been calculated from the slopes of these plots and are given in Table III. Also included for reference are values of $k_{Cl_2 \cdot^- + surfactant}$ obtained by combining k_7/k_8 with $k_{Cl_2 \cdot^- + pyrimidine}$ values from Table II. The intercepts of the competition plots, below the cmc, gave $G(-\text{pyrimidine})_0$ values identical, within experimental error, with those obtained in the absence of the surfactants.

For a given surfactant it may be seen that k_7/k_8 is always smaller above the critical micelle concentration than below it although the difference varies from a factor of 4.9 for the uracil–CTACl system to a factor of

Table III. Micellar Effects on the Relative Rates of $Cl_2\cdot^-$ Reactions with Surfactants and with Competitors, k_7/k_8, and on the Values of $k_{surf+Cl_2\cdot^-}$ Calculated from k_7/k_8[a]

	NaLS		Igepal CO-730		CTACl[d]	
	k_7/k_8	$k_{surf+Cl_2\cdot^-}$, M^{-1} sec^{-1}	k_7/k_8	$k_{surf+Cl_2\cdot^-}$, M^{-1} sec^{-1}	k_7/k_8	$k_{surf+Cl_2\cdot^-}$, M^{-1} sec^{-1}
Uracil						
Below cmc	1.0×10^{-1} [b]	3.5×10^6	68.3[c]	2.4×10^9	2.6×10^{-1}	9.1×10^6
Above cmc	1.5×10^{-3} [b]	5.3×10^4	5.04[c]	1.8×10^8	5.3×10^{-2}	1.9×10^6
Thymine[b]						
Below cmc	5.7×10^{-2}	4.0×10^6	17.5	1.2×10^9		
Above cmc	6.5×10^{-3}	4.6×10^5	0.58	4.0×10^7		
5-Chlorouracil[c]						
Below cmc	2.8×10^{-1}	2.8×10^6				
Above cmc	2.6×10^{-2}	2.1×10^5				
Cytosine						
Below cmc	4.2×10^{-1} [b]	4.2×10^6			3.35	3.0×10^7
Above cmc	2.0×10^{-2} [b]	2.0×10^5			-1.2×10^{-2}	
Cytidine						
Below cmc	2.5×10^{-1} [c]	1.0×10^6	15.1	6.0×10^7	2.2×10^{-2}	8.8×10^4
Above cmc	3.2×10^{-2} [c]	1.3×10^5	1.2	4.8×10^6	-1.2×10^{-3}	

[a] See text for experimental details. Concentration of competitors is kept at 1.2×10^{-4} M; some of these values differ from those cited in ref 2 partly because of obtaining additional data, and partly by using $G(-\text{pyrimidine})_0$ values extrapolated from the competition plots. [b] Solutions contained 0.50 M NaCl at pH 2.0 ($HClO_4$). [c] Solutions contained 0.10 M NaCl at pH 2.0 ($HClO_4$); above cmc, surfactant concentration exceeds the cmc by at least a factor of 5. [d] Solutions contained 0.10 M HCl.

-27.9 for the cytosine–CTACl system. Indeed, the sign of the slope of the competition plot changes for this latter system; that is, below the cmc, $k_{Cl_2\cdot^-+CTACl} > k_{Cl_2\cdot^-+cytosine}$, whereas above the cmc, $k_{Cl_2\cdot^-+CTACl} < k_{Cl_2\cdot^-+cytosine}$ (Figure 5). In the case of NaLS, it may be seen that combination of the directly determined values of $k_{Cl_2\cdot^-+pyrimidine}$ with k_7/k_8 results in a value of $k_{Cl_2\cdot^-+NaLS} = (3.5 \pm 0.7) \times 10^6$ M^{-1} sec^{-1} for four of the five pyrimidines. The good agreement here is an indication of straightforward competition and allows reasonable assignment of the value included in Table I. Rate constants for $Cl_2\cdot^-$ + NaLS above the cmc obtained in the same way range from 5.3×10^4 M^{-1} sec^{-1} for uracil to 4.6×10^5 M^{-1} sec^{-1} for thymine and show no such close agreement and are all considerably higher than $k_{Cl_2\cdot^-+NaLS}$ obtained by pulse radiolysis. A higher value taken from calculations involving k_7/k_8 implies that the overall destruction of the pyrimidine is decreased in the presence of micellar NaLS as it is difficult to envisage a mechanism by which presence of a pyrimidine would actually enhance $k_{Cl\cdot^-+surfactant}$. One may suggest then that degradation of thymine is most affected by NaLS and uracil the least. These effects must occur principally in secondary steps since pulse radiolysis has shown that the initial reactions with $Cl_2\cdot^-$ are small or unchanged in the presence of NaLS micelles. A similar approach to the Igepal CO-730 data, comparing values derived from k_7/k_8 with directly determined values of $k_{Cl_2\cdot^-+Igepal}$, indicates that Igepal substantially interferes with pyrimidine degradation *both* above and below the cmc. There is a considerable difference between values of $k_{Cl_2\cdot^-+surfactant}$ determined by the two methods. By contrast, comparison of steady-state and pulse radiolysis information for uracil and cytosine systems indicates that CTACl below the cmc has a very limited effect on destruction of pyrimidines. It has already been noted that negative slopes are obtained from plots of $1/G(-\text{cytosine})$ and $1/G(-\text{cytidine})$ *vs.* [CTACl]/[pyrimidine] above the cmc of CTACl. This, of course, can only mean an *increase* in cytosine and cytidine degradation in the presence of micellar CTACl which may come about either from an initial or subsequent step in the mechanism. As mentioned above, interference of transient absorption associated with CTACl prevents elucidation of the source of enhancement. However, changes in $k_{Cl_2\cdot^-+pyrimidine}$ observed by pulse radiolysis for these two substrates in the presence of micellar NaLS would suggest some possible solubilization of the substrate itself by CTACl, possibly at the surface. As has been shown in benzene-hydrated electron studies, this influence could well enhance the initial step of the mechanism.[10]

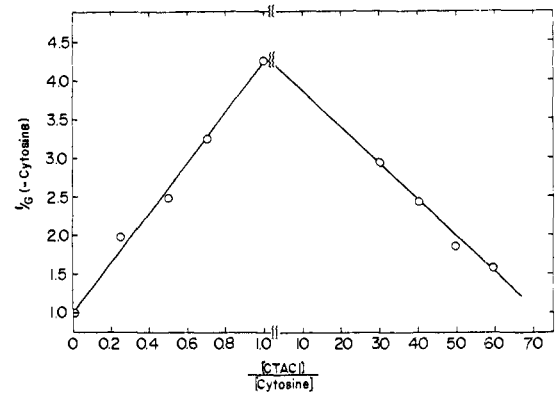

Figure 5. Competition plot for $Cl_2\cdot^-$ reaction with cytosine and with CTACl, [HCl] = 1.0×10^{-1} M. Concentration of CTACl above the cmc corrected for monomers.

Micellar or surfactant effects on the subsequent steps of the chain process may have several origins. Conceivably one or more of the radical intermediates are solubilized by the micelles with the resultant reaction rate differences. Since substrate solubilization by micelles is a dynamic process,[17] it can only significantly contribute if the binding constant for substrate–micelle association is appreciable and/or if the given radical reaction occurs on a time scale commensurate with or longer than the rate of substrate–micelle inter-

(17) E. J. Fendler and J. H. Fendler, *Phys. Org. Chem.*, 8, 271 (1970), and references cited therein.

action. Alternatively, it is quite possible that electron or radical transfer from the pyrimidine to surfactant interferes with the chain reaction thereby contributing to the decrease in the overall base destruction yield. Clearly the present data do not allow distinction among these possibilities.

Disappearance of Silyl Radicals in Silane. A Flash Photolysis–Electron Spin Resonance Kinetic Study[1]

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Abstract: Bimolecular self-reaction has been established as the dominant path for the disappearance of silyl and trimethylsilyl radicals dissolved in the corresponding silane. Rate constants were determined for trimethylsilyl radical self-reaction over the temperature range +20 to −82°. The activation parameters deduced from the temperature dependence of the rate constant and the rate constants themselves are typical for group IV radicals. Similar rate constants were found for the self-reaction of silyl radicals at −120 and −150°. Product studies indicate that dimerization is the principal self-reaction mechanism for trimethylsilyl radicals. A chain-carrying displacement of hydrogen atoms from a silane by a silyl or trimethylsilyl radical is not an important reaction under the present reaction conditions. The formation of disilane, the dimer of SiH_3, and the similarity of the self-reaction rates of silyl and trimethylsilyl radicals strongly suggest that direct dimerization is the mechanism for silyl radical self-reaction in solution.

The nature of the reactive intermediates formed upon pyrolysis and photolysis of silane, SiH_4, has been controversial for nearly 40 years.[2] Agreement has still not been reached on the question whether gas-phase pyrolysis of silane produces silylene, SiH_2, and molecular hydrogen, or alternatively silyl radicals, SiH_3, and hydrogen atoms. Mechanisms have been suggested involving either primary process to account for the formation of the observed products, disilane and molecular hydrogen.

Mechanism A

$$SiH_4 \longrightarrow SiH_2 + H_2 \quad (1)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \quad (2)$$

Mechanism B

$$SiH_4 \longrightarrow SiH_3 + H \quad (3)$$

$$H + SiH_4 \longrightarrow SiH_3 + H_2 \quad (4)$$

$$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \quad (5)$$

$$2SiH_3 \longrightarrow Si_2H_6 \quad (6)$$

To shed light on the interesting question, by what reaction paths do silyl radicals in silane solution disappear, it was decided to undertake a kinetic study. For the production of silyl radicals the convenient procedure of Krusic and Kochi was employed.[3] *tert*-Butyl peroxide is photolyzed to *tert*-butoxy radicals which abstract hydrogen atoms from silanes thus producing silyl radicals in solution.

The kinetic technique is similar to that developed by Weiner and Hammond.[4] The photolysis of *tert*-butyl peroxide is carried out with a modulated light source in order to facilitate signal averaging. Interference from signals due to long-lived free radicals is eliminated by use of a phase-sensitive detector to tune the detector response to the photolysis light frequency. Reaction mixtures thermostated with a gas stream are irradiated *in situ* in the microwave cavity of an electron spin resonance spectrometer.

In this manner growth and decay curves for the light-induced esr signal were collected and averaged. A typical decay curve for SiH_3 is shown in Figure 1. A similar technique has been used by Frangopol and Ingold[5a] and Watts and Ingold[5b] to measure the self-reaction rates of several organosilyl radicals. The apparatus for the present experiments has been described in connection with studies by Levanon and Weissman of the formation and decay of excited triplet molecules.[6,7]

While the goal of this investigation was to determine the mechanism for the disappearance of silyl radicals in silane solution, the mechanism cannot be determined from kinetic studies alone. Establishment of the rate law does not permit a choice between (1) a radical chain mechanism including disilane formation by *both* a chain-carrying "displacement"[8] *and* a bimolecular chain-terminating step; and (2) a nonchain process in which self-reaction of silyl radicals is the only process yielding disilane.

(1) This work has been carried out with financial support under contract from the U. S. Atomic Energy Commission. This is AEC Technical Report No. COO-1713-30.

(2) (a) For a review of the investigation of silane decomposition, see P. P. Gaspar and B. J. Herold, "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1971, Chapter 13. Important work has appeared since this reference went to press: (b) M. A. Ring, M. J. Puentes, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **92**, 4845 (1970); (c) P. John and J. H. Purnell, *J. Organometal. Chem.*, **29**, 236 (1971).

(3) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3938 (1969).

(4) (a) S. Weiner and G. S. Hammond, *ibid.*, **90**, 1659 (1968); (b) *ibid.*, **91**, 986 (1969).

(5) (a) P. T. Frangopol and K. U. Ingold, *J. Organometal. Chem.*, **25**, C9 (1970); (b) C. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

(6) H. Levanon, *Chem. Phys. Lett.*, **9**, 257 (1971).

(7) H. Levanon and S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4309 (1971).

(8) It should be noted that Professor Ring envisions silyl radicals inserting into an Si–H bond of silane while losing a hydrogen atom, a process which might be described as an insertion–elimination, in contrast with simple displacement.

insertion–elimination $\cdot SiH_3 + SiD_4 \longrightarrow SiH_2DSiD_3 + H$

displacement $\cdot SiH_3 + SiD_4 \longrightarrow SiH_3SiD_3 + \cdot D$