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- (29) The n_π^* orbital interacts with π_1 and π_2 ; however, gross populations of these latter two orbitals deviate markedly from 2. On the other hand, a two-electron stabilizing interaction of the type ($n_\pi - \pi^*$) can be calculated, and is found to be -8.01 kcal/mol at $\theta = 120^\circ$ and -7.05 kcal/mol at 110° . Since the magnitude of this attractive interaction is smaller at 110° than 120° , it cannot account for the observed relative stabilization of the 110° structure. The relative unimportance of a $F \cdots F$ attractive interaction also follows from the negative overlap populations between the two fluorine atoms (-0.0058 at 120° and -0.0104 at 110°) in the population analysis based upon atomic orbitals. This is consistent with the observations that the gross population of n_- is greater than that of n_+ , that of n_σ^* is greater than that of n_σ , and that of n_π^* is greater than that of n_π .
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- (32) There are some unusual bonding situations in which $(\Delta_{ij} - e^2 S_{ij}) > 0$, even when $S_{ij} > 0$. For details, see (a) M.-H. Whangbo and R. Hoffmann, *J. Chem. Phys.*, in press; (b) J. H. Ammeter, H.-B. Bürgi, J. C. Thibault, and R. Hoffmann, *J. Am. Chem. Soc.*, submitted for publication.

Formation and Disappearance of Free Radicals, and the Micellar Equilibrium in the Detergent Sodium 4-(6'-Dodecyl)benzenesulfonate

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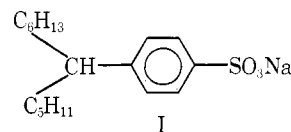
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Abstract: Aqueous N_2O -saturated solutions of sodium 4-(6'-dodecyl)benzenesulfonate were pulse irradiated with high-energy electrons and the formation and disappearance of radicals absorbing in the near-UV was observed. Most of the radicals were formed during the pulse by the addition of OH radicals from the radiolysis of water to the aromatic ring in the detergent molecules. A small fraction of the radicals was formed with a delay of some 200 μs . This effect is attributed to a slow reaction of alkyl radicals (formed by OH attack on the long aliphatic tail of the detergent molecules) with the aromatic ring. The radicals decay in a second-order process, the rate constant being $2k = 4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at an ionic strength of 0.1 M and at detergent concentrations below 2×10^{-3} M. Above this concentration, the rate constant becomes smaller. The dependence of the rate constant on the detergent concentration is understood in terms of the establishment of the micellar equilibrium $M_n \rightleftharpoons M_{n-1} + M \cdot$ for the radicals, followed by mutual deactivation of either two monomer radicals $M \cdot$ or a monomer radical with a radical in a micelle M_n . Deactivation between two radicals in micelles is too slow to contribute significantly to the disappearance of the radicals. Both the critical micelle concentration (2×10^{-3} M) and the rate constant ($4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) of the back reaction in the micellar equilibrium (at an ionic strength of 0.1 M, maintained by added $NaClO_4$) were derived in the analysis of the kinetic data on the disappearance of the radicals.

Introduction

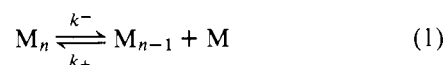
Micellar systems have often been used to solubilize complicated organic molecules in water and to study their reactions with free radicals (such as e_{aq}^- , OH, and H) produced by radiolysis of the solvent.¹ In most of these studies, the rate constant of reaction was determined using the method of pulse radiolysis, and in a few cases the fate of the radical that resulted from the attack of the solubilized molecule was also investigated.¹⁻⁵ However, the micelles themselves may be attacked by free radicals. OH radicals, for example, are reactive toward many detergents.¹ They generally react by abstracting a hydrogen atom from a C-H bond. The properties of the resulting radicals of the detergent have not yet been described.

In the present paper, the formation and especially the disappearance of radicals in aqueous solutions of sodium 4-(6'-dodecyl)benzenesulfonate (I) was investigated by using the method of pulse radiolysis. The solutions were irradiated under an N_2O atmosphere by a 50-ns pulse of high-energy electrons. Hydrated electrons from the radiolysis of water reacted



practically instantaneously according to $e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + OH$, and the OH radicals attacked the detergent to form organic free radicals. These radicals were detected by their optical absorption in the near-UV. Their bimolecular disappearance was studied under various concentration conditions.

It soon became evident in these studies that the kinetics of reactions of detergent radicals are strongly linked to the kinetics of the micellar systems involved. Let M be a molecule of the detergent and n the mean aggregation number of a micelle. A dynamic equilibrium exists:



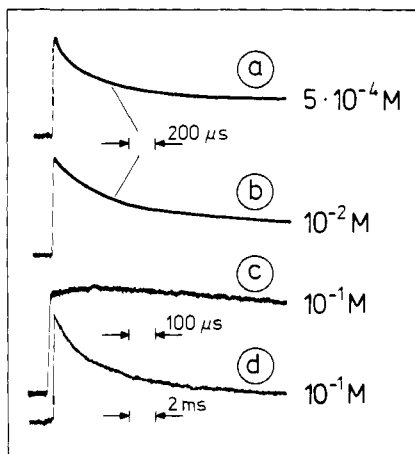


Figure 1. Oscillograms of the 320-nm absorption of pulsed solutions of sodium 4-(6'-dodecyl)benzenesulfonate at various concentrations of the detergent.

It is characterized by the rate constants k^- and k^+ for the exit and entrance of a monomer molecule. If we introduce a radical site into a small fraction of the molecules of the detergent, monomer radicals $M\cdot$ as well as micelled radicals $M_n\cdot$ (only one radical site in a micelle) will exist in the system. The rate constants k^- and k^+ may be expected to remain unchanged by the introduction of the radical site since this procedure affects only a small part of the long-chain detergent molecule. The residence time of a detergent radical in a micelle will be n/k^- . Provided that this time is essentially shorter than the time required for the chemical reaction of the radicals, the equilibrium between $M_n\cdot$ and $M\cdot$ is established before they disappear. $M_n\cdot$ and $M\cdot$ may have different reactivities toward either themselves or a third reactant.

The monomer-micelle equilibrium is perturbed by a temperature jump. In the earlier investigations, one relaxation time has been observed and rate constants for the dissociation of one molecule from the micelle have been derived from such data.^{6,7} The results from NMR measurements, however, could not be reconciled with a mechanism in which only one relaxation time is involved.⁸ In the more recent fast relaxation experiments, two processes have been observed.^{9,10} The shorter relaxation time is attributed to a shift of the mean aggregation number n of the micelles whose total number remains constant. The ratio k^-/n as well as the width of the distribution of n can be obtained from such experiments. The longer relaxation time is attributed to a change in the number of micelles. It will be shown below that the kinetic data obtained for the bimolecular disappearance of the radicals of the detergent can also be used to derive the important rate constants of the micellar equilibrium of eq 1.

Experimental Conditions and Results

Standard pulse radiolysis equipment with optical detection of the short-lived intermediates was used (4-MeV electrons: 50-ns pulse duration; dose per pulse 1500 rad). All solutions were bubbled with a stream of purified nitrous oxide for 0.5 h.

Oscillograms of the optical absorption at 320 nm of solutions containing the detergent at various concentrations are shown in Figure 1. The reaction of the OH radicals is fast enough to be practically completed after the pulse. The absorption which is recorded immediately after the pulse is attributed to the detergent radicals. Their spectrum at $t = 0$ ($t =$ time after the pulse) is shown in Figure 2. The maximum at 320 nm is typical for radicals of the hydroxycyclohexadienyl type which are formed in the fast addition of OH to aromatic rings.¹¹ The extinction coefficient of such radicals is generally slightly

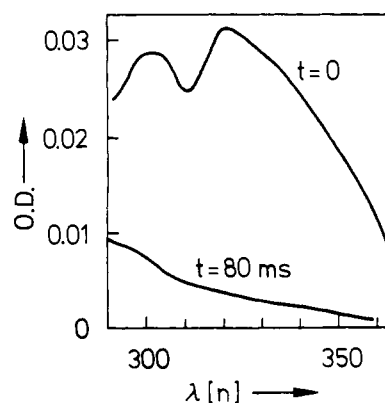


Figure 2. Absorption spectra immediately and 80 ms after the pulse. Detergent concentration 0.1 M.

higher than $3000 \text{ M}^{-1} \text{ cm}^{-1}$. Knowing the absorbed radiation energy and the yield of free radicals in N_2O -saturated solution ($G = 5.4$ radicals per 100 eV of absorbed radiation energy), one could calculate an extinction coefficient of $2700 \text{ M}^{-1} \text{ cm}^{-1}$ from the initial absorption after the pulse. It can thus be concluded that almost all of the OH radicals produced by the pulse are attached to micelles to form radicals of the hydroxycyclohexadienyl type. It cannot be excluded that a small fraction of the OH radicals attacked the detergent via H-atom abstraction at the long aliphatic chain. The alkyl radicals that would result from such an attack absorb at wavelengths substantially shorter than 320 nm. OH attack at the aromatic part of the detergent is more probable for two reasons:

(1) The rate constant for OH addition to aromatic rings is generally larger by at least one order of magnitude than for H abstraction from aliphatic chain.¹²

(2) The aromatic rings are located at the surface of the micelles while most of the aliphatic residues stick together inside; an OH radical residing mainly in the aqueous phase will therefore preferentially encounter the aromatic groups.

The absorption decays at long times after the pulse. However, as may be seen from curve c in Figure 1, a small increase in absorption occurs during about $200 \mu\text{s}$ after the pulse until the decrease takes over. At detergent concentrations below $2 \times 10^{-3} \text{ M}$, the increase was not observed. The general shape of the oscillogram did not change by varying the wavelength of observation. This indicates that the delayed absorption is caused by a species that has practically the same absorption spectrum as the one present immediately after the pulse.

At times much longer than those shown in Figure 1, the solutions had a constant residual absorption which became stronger with decreasing wavelength. Figure 2 also shows this absorption spectrum at 80 ms after the pulse. We ascribe it to a product that is formed in the deactivation of the cyclohexadienyl type radicals of the detergent. Experiments were also carried out with solutions of aromatic compounds that do not form micelles, i.e., with benzenesulfonic acid, *p*-isopropylbenzenesulfonic acid, *p*-*tert*-butylbenzenesulfonic acid, isopropylbenzene, and *tert*-butylbenzene. In all these cases, the absorption of the hydroxycyclohexadienyl-type radical was present immediately after the pulse. No delayed absorption was built up afterwards. In all these cases, a residual absorption remained at longer times.

The decay in the absorption (Figure 1) occurs more rapidly at higher doses of the pulse. The first half-life time of the decay was proportional to the reciprocal initial radical concentration at a given concentration of the detergent. The decay must therefore be attributed to the mutual deactivation of the detergent radicals. It can be recognized from the curves in Figure 1 that the radicals decay slower at higher concentrations of the detergent although the initial concentration of the radicals

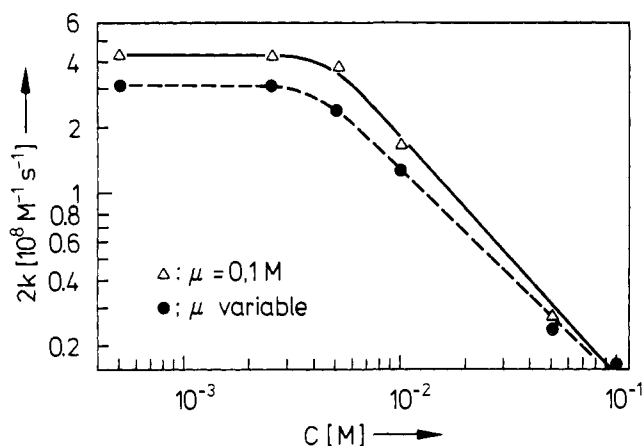


Figure 3. Double logarithmic plot of the rate constant $2k$ of disappearance of the radicals vs. the concentration C of the detergent. The ionic strength μ was either variable (O) or kept at 0.1 M (Δ) by adding NaClO_4 .

remains constant. Typical data, such as the initial radical concentration, the first half-life time and the calculated bimolecular rate constant $2k$ for the disappearance of the radicals, are compiled in Table I. It may also be mentioned that the decay of radicals formed in benzenesulfonic acid was independent of the concentration of this solute. Figure 3 shows the rate constant $2k$ as a function of the concentration C of the detergent. One set of experiments was carried out without NaClO_4 as additive, i.e., with solutions of different ionic strengths. In the second set, NaClO_4 was added in such quantities as to maintain an ionic strength of 0.1 M. Under these conditions, the salt effect on the rate constant did not distort its dependency on the detergent concentration C . As may be seen from Figure 3, $2k = 4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, if $C = 2 \times 10^{-3} \text{ M}$. At larger concentrations, $2k$ becomes smaller. At concentrations substantially above $2 \times 10^{-3} \text{ M}$, i.e., in the range between 0.02 and 0.1 M, $2k$ is proportional to $1/C$.

Discussion

A significant difference in reactivity was found between cyclohexadienyl radicals formed in the detergent sodium 4-(6'-dodecyl)benzenesulfonate and in a compound that does not form micelles such as benzenesulfonic acid. While the radicals of benzenesulfonic acid disappear with a bimolecular rate constant that is not dependent on the benzenesulfonic acid concentration, the radicals of the detergent possess a rate constant that decreases with increasing detergent concentration above $2 \times 10^{-3} \text{ M}$. This effect is explained by the fact that micelles are formed only above a certain critical micelle concentration, cmc. This critical concentration apparently amounts to $2 \times 10^{-3} \text{ M}$ for sodium 4-(6'-dodecyl)benzenesulfonate. Above this concentration, an increasing fraction of the radicals is formed in the micelles and not in monomer molecules of the detergent. Radicals in micelles M_n cannot react with each other as fast as monomer radicals M , since the negatively charged micelles repel each other.

The lifetimes of the radicals amount to some milliseconds (Table I) under our experimental conditions. The relaxation time of micellar equilibria has been found to be some 10^{-5} – 10^{-4} s for ionic detergents.⁹ We may thus expect the equilibrium between radicals in micelles and monomer radicals to be established before the radicals disappear by reacting with each other. The following deactivation processes ought to be considered (P = products):



Table I. Data on the Disappearance of the Detergent Radicals (μ Variable)

Concn of detergent, M	Initial radical concn, M	First half-life time, ms	$2k$, $\text{M}^{-1} \text{ s}^{-1}$
1×10^{-1}	1.17×10^{-5}	5.22	1.6×10^7
5×10^{-2}	1.08×10^{-5}	3.80	2.4×10^7
1×10^{-2}	8.84×10^{-6}	0.83	1.4×10^8
5×10^{-3}	8.67×10^{-6}	0.50	2.3×10^8
2.5×10^{-3}	7.33×10^{-6}	0.44	3.1×10^8
3×10^{-4}	4.83×10^{-6}	0.65	3.2×10^8

The total rate of disappearance of radicals is

$$-d[R]/dt = 2k_2[M \cdot]^2 + 2k_3[M \cdot][M_n \cdot] + 2k_4[M_n \cdot]^2 \quad (5)$$

where $[R] = [M \cdot] + [M_n \cdot]$ is the total radical concentration and the $2k$'s are the bimolecular rate constants of the respective processes of deactivation. $[M \cdot]$ and $[M_n \cdot]$ may now be substituted by

$$[M \cdot] = \frac{cmc}{C} [R] \quad (6)$$

$$[M_n \cdot] = \frac{C - cmc}{C} [R] \quad (7)$$

where C is the total concentration of detergent molecules. The ratio $[R]/C$ was always smaller than 0.01. In writing eq 6 and 7, use was made of the fact that the concentration of monomer detergent molecules in the micellar equilibrium of eq 1 is always equal to the critical micelle concentration at $C > cmc$.¹³ The molar concentration of micelles is $(C - cmc)/n$, and the probability for finding one molecule in a micelle with a radical site is equal to $[R]n/C$. After substitution one obtains

$$\begin{aligned} -\frac{d[R]}{dt} &= \frac{2k_2(cm c)^2 + 2k_3cm c(C - cm c) + 2k_4(C - cm c)^2}{C^2} [R]^2 \end{aligned} \quad (8)$$

The fraction on the right-hand side of eq 8 is equal to the observed bimolecular rate constant for the disappearance of the radicals.

$$2k = \frac{2k_2(cm c)^2 + 2k_3cm c(C - cm c) + 2k_4(C - cm c)^2}{C^2} \quad (9)$$

At concentrations $C < cmc$, no radicals $M_n \cdot$ are present. The observed rate constant $2k$ is equal to $2k_2$ under these conditions. At an ionic strength of 0.1 M of the solution, $2k_2 = 4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is obtained from Figure 3. After correcting for the kinetic salt effect by using the Brønsted-Bjerrum equation, a rate constant $2k = 2.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is obtained for the mutual deactivation of two monomer radicals of the detergent.

At very high concentrations of the detergent, reaction 4 should be the predominant process through which the radicals disappear. Under these conditions, $2k$ should become independent of the detergent concentration and be equal to $2k_4$. However, even at the highest concentration of 0.1 M used in the experiments of Figure 3, no indication was obtained that the rate constant would reach a lower constant level. It must thus be concluded that $2k_4$ is very small and that reaction 4 does practically not occur under our concentration conditions. The linear relationship between $2k$ and C in the range between $C = 10^{-2}$ and 10^{-1} M in Figure 3 indicates that reaction 3 is here the main process of deactivation. An analysis of the curve

for constant ionic strength in Figure 3 yielded a value of $8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $2k_3$. In this analysis, the term $2k_4(C - \text{cmc})^2/C^2$ was neglected, and a value of $2 \times 10^{-3} \text{ M}$ was used for cmc. At an ionic strength of zero, $2k_3$ would be expected to be substantially smaller.

The rate of reaction of monomer radical with a radical in a micelle is thus found to be larger by almost a factor of 2 than the rate of reaction of two monomer radicals. This finding seems surprising at first sight since the micelle should exert a strong repulsive force on the negatively charged monomer radical because of its large negative surplus charge. However, one can imagine that the long aliphatic tail of the monomer radical promotes the capture of the radical by the micelle. As the monomer radical has approached the micelle at a certain distance, the end of its aliphatic residue may touch the hydrocarbon-like interior of the micelle during its varied thermal movement. The aliphatic end is now anchored at the micelle. The chain contraction of the aliphatic residue into the interior of the micelle facilitates closer approach of radical group of the detergent molecule until mutual deactivation with the radical already present in the micelle occurs. Reaction 3 is thus understood in terms of the capture of a monomer radical by a micelle, i.e., in terms of the back reaction of the micellar equilibrium of eq 1. Under these circumstances one may identify the rate constant $k_3 = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ with the rate constant k^+ of the micellar equilibrium.

The equilibrium constant of eq 1 is equal to the cmc:

$$\text{cmc} = k^-/k^+ \quad (10)$$

Using $\text{cmc} = 2 \times 10^{-3} \text{ M}$ and $k^+ = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ one obtains $k^- = 8 \times 10^5 \text{ s}^{-1}$. We have thus achieved a complete determination of the rate constants that characterize the micellar equilibrium by using only the kinetic data for the mutual deactivation of the detergent radicals. These results may be compared with the results from relaxation measurements which have recently been carried out by Hoffmann and his co-workers and which will be published in detail elsewhere. They obtained a value of k^-/n of $1.3 \times 10^4 \text{ s}^{-1}$, and also found a cmc of $2 \times 10^{-3} \text{ M}$ by carrying out conductivity measurements. The aggregation number n of anionic micelles carrying a dodecyl residue and an aromatic group lies between 25 and 60.¹⁴ k^- values between 3.3×10^5 and $7.8 \times 10^5 \text{ s}^{-1}$ are therefore expected from the k^-/n ratio determined by the relaxation method. The agreement with our value of $8 \times 10^5 \text{ s}^{-1}$, which is possibly an upper limit for the reasons discussed above, is very satisfying.

The concentration at which $2k$ starts to decrease in Figure 3 is practically independent of the ionic strength of the solution. This appears surprising since it is known from the work on n -alkyl sulfonates that the cmc decreases with increasing ionic strength. It may be that this decrease is less pronounced for the detergent used in the present work. Furthermore, k_3 will be strongly dependent on the ionic strength at low tenside concentrations. The effects that are caused on the overall rate constant $2k$ by a decrease in cmc and an increase in k_3 may to a certain degree counterbalance each other.

The above mechanism for the mutual deactivation of ten-sided radicals resembles certain aspects of the theory of emulsion polymerization.¹⁵ Large growing radicals surrounded by a layer of ten-sided molecules and containing monomer

molecules are important intermediates of such polymerization. They cannot react with each other because of their mutual repulsion. A smaller radical may, however, enter the polymer-ten-sided agglomerate and destroy the large radical in it. On the other hand, a smaller radical may also happen to enter a deactivated polymer-ten-sided cluster and restart polymerization there.

An explanation for the delayed formation of a small fraction of the detergent radicals absorbing at 320 nm may finally be proposed. As mentioned in the Experimental Section, a small fraction of the OH radicals may not have reacted with the aromatic groups in the micelles of sodium 4-(6'-dodecyl)benzenesulfonate, but may have attacked the aliphatic residue. An alkyl radical formed this way may subsequently undergo a reaction with an aromatic group in the same micelle to yield an additional radical of the cyclohexadienyl type. This reaction could be either the addition of the alkyl radical to the ring or the transfer of a hydrogen atom. The optical absorption of the cyclohexadienyl-type radicals formed would be almost indistinguishable from that of the corresponding hydroxycyclohexadienyl radicals. The reaction between an alkyl radical and the aromatic ring of a molecule can generally not be observed in pulse radiolysis studies since it is too slow. That this reaction may occur rather rapidly in the micelles is explained by the high local concentration of the aromatic rings in the micelles of sodium 4-(6'-dodecyl)benzenesulfonate. Using a first half-life time of 200 μs for the alkyl radicals and a local concentration of the aromatic rings of 2 M, one estimates the bimolecular rate constant of this reaction to be of the order of 10^3 s^{-1} .

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