# On the Reduction of Dimensionality in Radical Decay Kinetics Induced by Micellar Systems

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**Abstract:** The dismutation reaction of $Br_2^-$ ion radicals in aqueous solution was studied in the presence of micellar cetyltrimethylammonium bromide (CTAB) by pulse radiolysis technique. Two kinetic processes involving the $Br_2^-$ radicals were identified: two-dimensional intramicellar surface diffusion and three-dimensional intermicellar (or solution bulk type) diffusion with respective rate constants of $2.1 \times 10^6$ s$^{-1}$ and $1.46 \times 10^9$ M$^{-1}$ s$^{-1}$. The CTAB/$Br_2^-$ system represents the first example in which two kinetic components of a diffusion-controlled reaction differing in dimensionality of reaction space can be distinguished. Reduction of dimensionality dramatically increases the probability of reaction. Random-walk theory for two- and three-dimensional lattices with traps is invoked to explain these results.

## Introduction

The rate of various chemical processes in solution is enhanced by the presence of organized molecular assemblies, such as micelles or membrane systems.[2] Among the various factors contributing to the catalytic effects, hydrophobic and electrostatic interactions of the amphipathic surface of the aggregates with reactive species in the aqueous phase are crucial.[3] Frequently, a large fraction of the reactant is adsorbed in the interface separating the lipoidic part of the aggregate from the aqueous environment. When the reactive species are distributed both on the surface of the aggregates and in the aqueous phase, two alternative mechanisms of bimolecular reactions differing in the dimensionality of reaction space are possible. These are two-dimensional surface diffusion and the more usual three-dimensional diffusion, the latter type characteristic of homogeneous bulk reactions. Assessment of the influence of the dimension of reaction space on the rate of chemical reactions is of kinetic and biological importance. For this reason we have initiated research on micellar model systems to investigate situations where direct examination and separation of these two diffusional processes are possible. The first observation of this kind is reported in the present paper for the case of the $Br_2^-$ ion radical in (cationic) micellar cetyltrimethylammonium bromide solution. In the dismutation reaction of this species, the surface and bulk diffusion can be separately identified. The relative rates of the two processes can be interpreted theoretically using predictions derived from a theory of random walk on two- and three-dimensional lattices with traps.

## Experimental Section

**A. Materials.** Cetyltrimethylammonium bromide (CTAB) was obtained from Fluka (purum) and was recrystallized several times from methanol/ether mixtures. Sodium bromide (Merck, ultrapure) was used as supplied. The solutions were prepared with triply distilled water and freed from air by flushing with nitrous oxide for at least 15 min.

**B. Apparatus.** Pulse radiolysis with optical methods of detection was used to produce bromide anion radicals ($Br_2^-$) and to monitor their reaction. The absorption of the solution was recorded as a function of time from $10^{-8}$ to $10^{-2}$ s. Transients were produced with either a 5-20-ns pulse from a linear accelerator or a 2-$\mu$s pulse from a Van de Graaff accelerator. Experimental details concerning these techniques have been published elsewhere.[4]

## Results

The following experiments were carried out with $N_2O$ saturated aqueous solutions of $2 \times 10^{-2}$ M NaBr in the presence and absence of $5 \times 10^{-3}$ M CTAB. In this system the electron pulse from the accelerator initiates a well-known series of rapid reactions,[5,6] leading to the formation of Br atoms during the time of the pulse. For every 100 eV of energy absorbed by the system, 5.5 Br atoms are formed.[5b,c] Thus by means of pulse radiolysis technique it is possible to produce within the short period of 5–20 ns a definite concentration of Br atoms, about $3 \times 10^{-6}$ to $30 \times 10^{-6}$ M depending on the pulse width. The subsequent reactions of Br atoms have also been well characterized.[5b,c,6] They involve formation of $Br_2^-$ radicals

$$Br\cdot + Br^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2^- \qquad (1)$$

followed by the dismutation reaction

$$Br_2^- + Br_2^- \xrightarrow{k_2} Br_3^- + Br^- \qquad (2)$$

Since the equilibrium constant for (1), $K_1 = k_1/k_{-1}$, is $2.5 \times 10^5$ M$^{-1}$ (see ref 5b), conversion of Br atoms into $Br_2^-$ radicals will be practically quantitative at the bromide ion concentration employed in our experiments. The tribromide anion formed in reaction 2 dissociates subsequently into bromine and bromide ion.

$$Br_3^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Br_2 + Br^- \qquad (3)$$

The equilibrium of reaction 3 ($K_3 = 0.062$) is established within about 100 ns, since the back reaction occurs near the diffusion controlled rate.[5b]

$Br_2^-$ and $Br_3^-$ are readily distinguishable by their characteristic absorption spectra in the near-ultraviolet region. The $Br_2^-$ radical anion has an absorption maximum at 360 nm and an extinction coefficient of 9600 M$^{-1}$ cm$^{-1}$ at this wavelength.[5b] The absorption of $Br_3^-$ shows a maximum at 270 nm with an extinction coefficient of $3.9 \times 10^4$ M$^{-1}$ cm$^{-1}$.[5b] Since both spectra show very little overlap at their respective maxima, the kinetic behavior of $Br_2^-$ and $Br_3^-$ can be inferred from monitoring the absorbance of the solution at 270 and 360 nm.

Figure 1 shows the absorption at these two wavelengths as a function of time for the irradiated aqueous CTAB-NaBr system. The upper trace indicates an immediate increase in absorbance at 360 nm and a further growth occurring within a period of 100 ns. This corresponds to the formation of Br atoms during the pulse and their subsequent conversion into $Br_2^-$ according to reaction 1. The lower trace shows the growth of the $Br_3^-$ anion at 270 nm over a time of several microseconds. The fast formation of $Br_2^-$ is expected from the value of

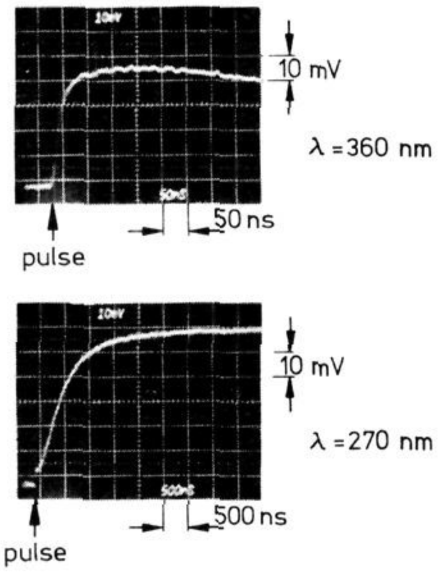

**Figure 1.** Oscilloscope traces of the growth of $Br_2^-$ radicals (upper curve) and $Br_3^-$ ions (lower curve) in aqueous 0.02 M NaBr and $5 \times 10^{-3}$ M CTAB solution saturated with $N_2O$. Upper curve: Abscissa, 50 ns per large division, ordinate, 6% absorption change per large division; wavelength, 360 nm. Lower curve: Abscissa, 500 ns per large division; ordinate, 6% absorption charge per large division; wavelength, 270 nm. Pulse width: 20 ns.

the rate constant $k_1$ which approaches the limit for a diffusion-controlled reaction. A comparison of the aqueous NaBr system (left column, Figure 2) with the aqueous CTAB–NaBr system (middle column, Figure 2) indicates an unusual effect induced by the CTAB micelles on the subsequent reactions of $Br_2^-$. The kinetic behavior of the $Br_2^-$ species in the latter system is characterized by a two-step decay. The fast process, indicated by the rapid decrease in the 360-nm absorption, is completed within 2 μs and is followed by a second much slower absorption decay occurring over a period of more than 100 μs. Concomitantly with these events, one observes a pronounced increase in the absorption at 270 nm (right column, Figure 2) which consists also of two well-separated components.

In the absence of micelles (left column, Figure 2), the transient absorption at 360 nm decays in a smooth fashion and plots of the reciprocal absorbance vs. time yield linear relations from which a second-order rate constant $k_2 = 2.4 \times 10^9$ $M^{-1}$ $s^{-1}$ is derived. When this value is corrected for the salt effect of NaBr, it is in close agreement with the literature value $k_2 = 1.8 \times 10^9$ $M^{-1}$ $s^{-1}$ (see ref 5b,c). The fast components of the 360-nm decay and the 270-nm growth were found to obey first-order kinetics. Conversely, the slower reaction of $Br_2^-$ was found to obey second-order kinetics similar to the results obtained in the absence of CTAB. The rate constants for the two processes derived from this analysis are $k_2(\text{fast}) = 2.1 \times 10^6$ $s^{-1}$ and $2k_2(\text{slow}) = 1.6 \times 10^9$ $M^{-1}$ $s^{-1}$. As the pulse width decreases, and therefore the initial $Br_2^-$ concentration, the fast decaying fraction of the 360-nm absorption also diminishes as will be seen in Figure 2. The same observation is true for the fast and slow component of $Br_3^-$ formation.

Apart from the kinetic features which distinguish micellar from micelle-free NaBr solutions, a further conspicuous difference exists with respect to tribromide anion concentrations formed via the $Br_2^-$ disproportionation. From a consideration of reactions 2 and 3, one expects in aqueous solution that one-eighth of the initially produced $Br_2^-$ should be converted into $Br_3^-$. As the extinction coefficient of $Br_3^-$ at 270 nm is about four times larger than that of $Br_2^-$ at 360 nm, the conversion of $Br_2^-$ into $Br_3^-$ should be associated with a final 270-nm absorbance corresponding to about half of the initial 360-nm transient absorbance. While these expectations are fulfilled in aqueous NaBr solutions, much higher yields of $Br_3^-$ are observed in the presence of CTAB. This behavior is illustrated in Figure 3, which shows pulse radiolysis results from Van de Graaff experiments. The dashed line represents the transitory spectrum present immediately after the 2-μs electron pulse. It shows the $Br_2^-$ peak at 360 nm and a second peak at 270 nm which is due to the fast formation of $Br_3^-$ during the accelerator pulse. The subsequent reaction of $Br_2^-$ produces a substantial increase in the absorbance at 270 nm. The final yield of $Br_3^-$ corresponds to almost one-half of the initially produced $Br_2^-$ concentration, indicating that dissociation of $Br_3^-$ into $Br_2$ and $Br^-$ according to reaction 3 does not occur to any appreciable extent in the CTAB micellar solution.

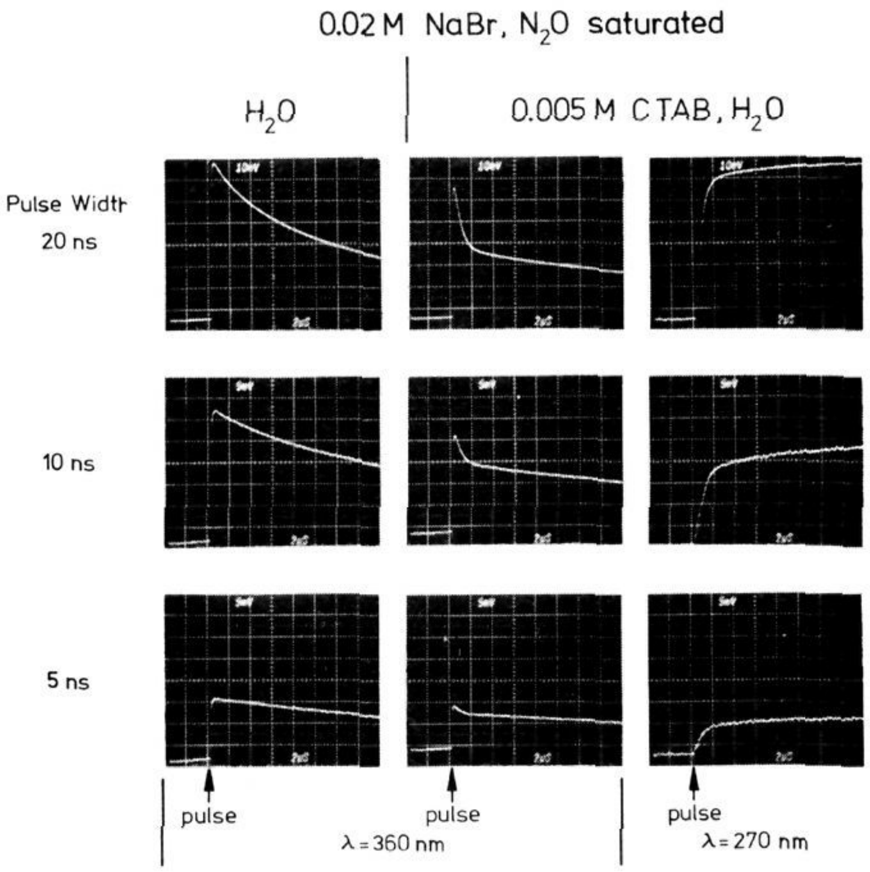

**Figure 2.** Oscilloscope traces of the kinetics of $Br_2^-$ radicals (left and middle columns) and $Br_3^-$ ions (right column). Left column: aqueous 0.02 M NaBr saturated with $N_2O$, wavelength 360 nm. Middle column: aqueous 0.02 M NaBr and $5 \times 10^{-3}$ M CTAB saturated with $N_2O$, wavelength 360 nm. Right column: aqueous 0.02 M NaBr and $5 \times 10^{-3}$ M CTAB saturated with $N_2O$, wavelength 270 nm. Upper row: Abscissa, 2 μs per large division; ordinate, 6% absorption charge per large division; pulse width, 20 ns. Middle row: Abscissa, 2 μs per large division; ordinate, 3% absorption charge per large division; pulse width, 10 ns. Lower row: Abscissa, 2 μs per large division; ordinate, 3% absorption charge per large division; pulse width, 5 ns.

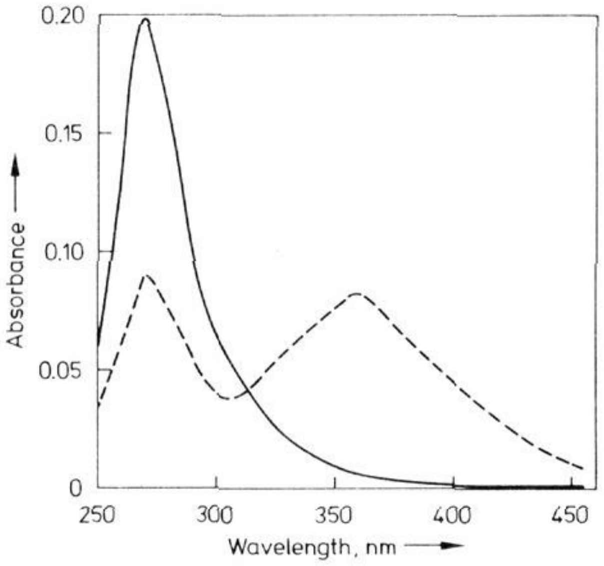

**Figure 3.** Transient absorption spectra obtained immediately (- - - curve) and 7 ms (—— curve) after the 2-μs Van de Graaff pulse in aqueous 0.02 M NaBr and $5 \times 10^{-3}$ M CTAB solution saturated with $N_2O$.

## Discussion

**A. Intramicellar Surface Reactions vs. Intermicellar and Solution Bulk Reactions.** Evidence for intramicellar surface reaction vs. intermicellar and solution bulk reactions is, in part, substantiated by statistical arguments. The possible distribution of $Br_2^-$ radicals among the micellar aggregates is con-

**Table I.** Comparison of the Fast Component of $Br_2^-$ Radicals and $Br_3^-$ Ions Kinetics in Micellar CTAB Solution with a Statistically Predicted Distribution

| Exptl runs | $[Br_2^-]_0$ $\times 10^6$ M | Fractions of $Br_2^-$ decay via fast component | Fractions of $Br_3^-$ growth via fast component | Theoret prediction[a] |
|---|---|---|---|---|
| High dose (20-ns pulse width) | 26.9 | 0.61 | 0.47 | 0.55 |
| Medium dose (10-ns pulse width) | 7.32 | 0.30 | 0.35 | 0.32 |
| Low dose (5-ns pulse width) | 3.12 | 0.16 | 0.27 | 0.30 |

[a] Ratio of micelles with two or more $Br_2^-$ to those with one or more $Br_2^-$.

sidered first. The concentration of micelles in the solution is given by the expression:

$$[\text{micelles}] = ([\text{CTAB}] - \text{CMC})/n$$

where [CTAB] is the total surfactant concentration, and CMC and $n$ are the critical micelle concentration and the aggregation number of the micelle, respectively. Both CMC and $n$ are affected by the ionic strength of the solution. Using a logarithmic relation to correct for this dependency,[7] the CMC of CTAB in the presence of 0.02 M NaBr is $2.24 \times 10^{-4}$ M. A value of $n = 221$ was derived by interpolation of the literature data.[8] From these values and [CTAB] = $5 \times 10^{-3}$ M, the concentration of micellar aggregates, which was kept constant throughout the experiments, is $2.16 \times 10^{-5}$ M.

Table I presents the initial $Br_2^-$ concentrations produced after each of the three different pulse widths employed in the experiments. The $Br_2^-$ radicals are expected to be more strongly associated with the surface of the CTAB micelles than are the $Br^-$ counterions. The absorption of counterions to a micellar surface is known to follow the lyotropic (Hoffmeister) series.[9] Since $Br_2^-$ is about twice as large as $Br^-$ and has a lower charge density, it is expected to display a much higher affinity for the micellar surface than the bromide ion. We therefore have made the simplifying assumption that the distribution of $Br_2^-$ is restricted to the surfaces of the micellar aggregates.[10] From the total number of micelles having $Br_2^-$ radicals adsorbed on the surface, a certain fraction will have single associations and the remainder will have multiple associations with $Br_2^-$. The ratio of micelles with two or more $Br_2^-$ radicals to those with one or more $Br_2^-$ radicals is listed in the last column of Table I. These values indicate that an appreciable fraction of CTAB micelles, depending on the accelerator dose, have more than one $Br_2^-$ adsorbed on their surface. Among the micelles with multiple $Br_2^-$ associations, the majority will have only two $Br_2^-$ radicals bound to them. Thus the disproportionation of $Br_2^-$ in CTAB micellar solution is envisaged to proceed via three different pathways as illustrated schematically in Figure 4. In micelles with two $Br_2^-$ associations, intramicellar reaction involving two-dimensional surface diffusion is feasible, as discussed in the next section. Since this reaction occurs between pairs of $Br_2^-$ radicals on single host aggregates, it should obey first-order kinetics. The remaining portion of the $Br_2^-$ radicals are consumed in intermicellar, micellar-bulk or bulk reactions involving three-dimensional diffusion. The kinetics of such a process are described by a second-order rate law.

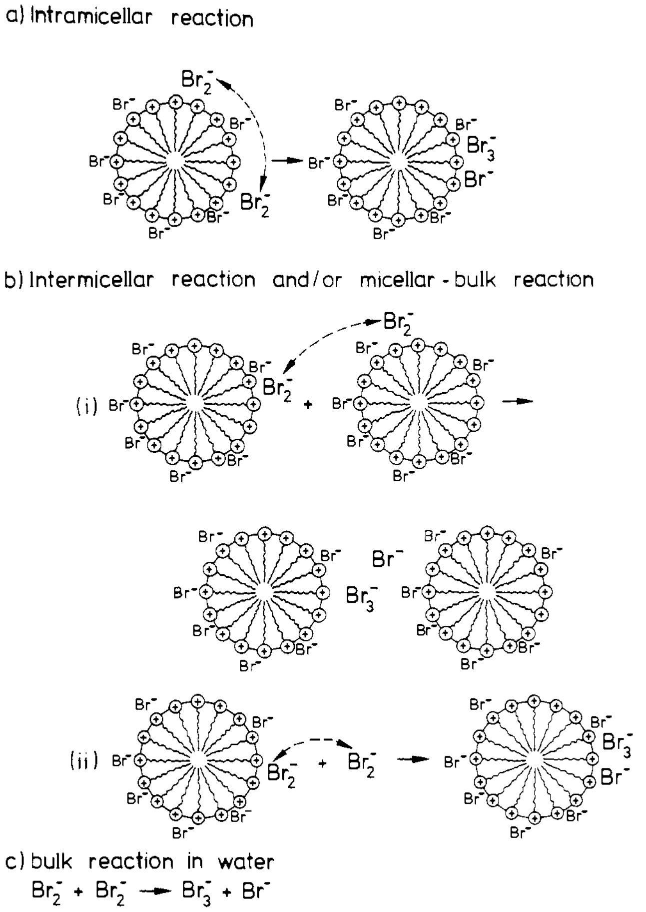

**Figure 4.** Schematic illustration of possible pathways for the dismutation reaction of $Br_2^-$ ion radicals in micellar CTAB solution.

Comparison of the second column with the last two columns in Table I shows the close correlation between the fractions of $Br_2^-$ anion radicals consumed and the $Br_3^-$ anions formed in the initially fast process, and the statistically predicted fractions of aggregates with multiple associations. It is concluded, therefore, that the initially fast $Br_2^-$ decay originates from surface reactions of two $Br_2^-$ radicals associated with a single micelle (process a, Figure 4), while the slow component represents intermicellar, micellar-bulk, and bulk $Br_2^-$ reactions (processes b and c, Figure 4). The fact that the fast $Br_2^-$ reaction obeys first-order kinetics and the slow one follows a second-order rate law is in agreement with these conclusions. Also consistent with this view is the enhanced absorbance of the $Br_3^-$ ions in the aqueous CTAB-NaBr system relative to the CTAB-free solution. Because of the high local $Br^-$ concentration in the CTAB micellar Stern layer, the probable site of $Br_3^-$ formation, the equilibrium situation in reaction 3 is shifted far to the left.

**B. Two-Dimensional vs. Three-Dimensional Diffusion Processes: Effects of Reduction of Dimensionality on Reaction Rates.** In this section we suggest a possible interpretation of the trends observed in the experimental rate constants and present estimates to assess the validity of this interpretation. To begin, we note that Adam and Delbrück[11] in 1968 explored mathematically the possibility that "organisms handle some of the problems of timing and efficiency, in which small numbers of molecules and their diffusion are involved, by reducing the dimensionality in which diffusion takes place from three-dimensional space to two-dimensional surface diffusion". In their study these authors proved a theorem substantiating their conjecture that, for the case of small targets, a reduction of dimensionality from three to a lower one is clearly advantageous for diffusion-controlled processes. In this section, we examine the possibility that the significant difference found experimentally in the rate of reaction of $Br_2^-$ radicals for intermicellar vs. intramicellar processes is due to the fact that, in the latter case, a reduction in dimensionality of the reaction space from three dimensions to two has been achieved by the CTAB micellar system. Although more detailed calculations will be reported in a later contribution, we use here theoretical results already in the literature to assess the rasonableness of this interpretation.

To formulate the problem, suppose we focus attention on a single $Br_2^-$ radical. For definiteness, we assume that this radical is fixed in position, or if it happens that this $Br_2^-$ radical is bound to a CTAB micelle, that the micelle is positioned at the center of a coordinate system. Suppose now we identify a second $Br_2^-$ radical, which may be present in the bulk solution or affixed to a second CTAB micelle. If we regard reaction to take place upon encounter of the two $Br_2^-$ radicals, the question arises as to the lifetime of the second $Br_2^-$ radical before it is "trapped" by the first one—with subsequent reaction to yield $Br_3^-$ and $Br^-$. Now recent theoretical work on the relaxation of the continuum approximation in the theory of electrolytes[12] has indicated that the Coulomb potential experienced by a counterion in the neighborhood of a central ion damps rapidly to zero as one moves away from the central ion. Hence, if we exclude from our considerations the immediate electrostatic neighborhood of the central charged species, we may regard the kinetic motion of the second $Br_2^-$ radical in solution as essentially random. Then, from the standpoint of lattice statistics, the problem is: Given a lattice which contains a trap at some fixed point, if a random walker has the same probability of starting from any nontrapping point, how many steps must he take on the average before being trapped? This problem has been solved by Montroll in a variety of situations[13] (different lattice geometries, different dimensions, etc.), and in our discussion we shall use his results. In three dimensions, the basic formula derived is that for the average number $\langle n \rangle_3$ of steps required for a random walker on a perfect lattice of $N$ points to go from the origin to a typical point $(l_1, l_2, l_3)$ for the first time (for one diffusing particle and one trap the choice of origin is obviously immaterial). Montroll has determined that

$$\langle n \rangle_3 \sim N[\phi(0,1) + (3/2\pi l) + o(1/l^2)]$$

where $\phi(0,1) = 1.516\ 386\ 0591$ and $l^2 = l_1^2 + l_2^2 + l_3^2$. Since the motion of the second $Br_2^-$ radical will be random only at distances somewhat removed from the central $Br_2^-$ radical, we may safely use the asymptotic estimate (valid for $l > 25$)

$$\langle n \rangle_3 \sim N\phi(0,1)$$

or, since from the formulation of the problem $N = 1/c$, where $c$ is the trap concentration,

$$\langle n \rangle_3 \sim 1.51638/c$$

This estimate for $\langle n \rangle_3$ will be used in a subsequent paragraph to determine a lower bound on the average number of steps required before the second $Br_2^-$ radical is trapped.

Turning next to a consideration of the intermicellar kinetics, let us assume that the two $Br_2^-$ radicals are held to the CTAB surface by forces sufficiently strong to guarantee adsorption but also sufficiently weak to permit diffusion along the surface. To give the simplest characterization of these forces, we begin by noting that Hartley[14] has estimated the fraction of gegenions adhering to the micellar surface when aggregation first sets in to be approximately 0.75. Using his estimate, we determine that a CTAB micelle of 221 molecules would have a net charge of about 55 units or, in other words, ca. 55 free sites on the CTAB surface would be available to the $Br_2^-$ radicals for adsorption. On statistical grounds, there may exist many possible configurations of the two $Br_2^-$ radicals which would differ little in free energy. Fluctuations in the configurations of the $Br_2^-$ radicals are therefore possible, and a rationale for surface diffusion is thus provided. In fact, the picture just described is similar in spirit to one suggested in 1952 by Kirkwood and Shumaker[15] in their theory of dipole moment fluctuations in protein solutions; these authors were able to show that fluctuations in the configurations of protons could account for the dielectric increments of many proteins and, as well, could make an important contribution to interprotein forces. Within the context of the present discussion, we can obtain some first estimates on the possible importance of surface diffusion in intramicellar kinetics by using some further results of Montroll. Suppose for definiteness we assume that one of the $Br_2^-$ radicals is positioned at some point on the CTAB micellar surface, and then consider the motion of the second $Br_2^-$ radical relative to this "trap". Locally, the surface on which the diffusing $Br_2^-$ radical moves may be regarded as two-dimensional; here, we specify this surface to be a lattice, with the sites identified as the free sites on the CTAB surface. Montroll has determined for a two-dimensional lattice of unit cells, each containing one trap and $N - 1$ nontrapping points, and infinite in extent that

$$\langle n \rangle_2 = \frac{1}{1-c}\left[\frac{\ln c}{\pi c} + \frac{0.19506}{c} - 0.11696 - 0.05146c + \ldots\right]$$

This estimate for $\langle n \rangle_2$ will be used below to determine the average number of steps required before the $Br_2^-$ radical diffusing on the micellar surface is trapped.

In order to determine $\langle n \rangle_2$ and $\langle n \rangle_3$ from the expressions given above, it is necessary to determine $c$, the concentration of traps, in each case. This, in turn, requires an estimate of the number of available lattice points. In the *two-dimensional* case, this number is simply the number of available head groups on the surface of the micelle. For the system under study, viz. a CTAB "unit cell" with ca. 55 free sites, the trap concentration would be $c = 1/N = 1/55$ traps per total number of lattice sites. The prediction, then, is that in the *intramicellar* case, the mobile $Br_2^-$ radical takes $\langle n \rangle_2 \sim 82$ steps on the average before being trapped by the first $Br_2^-$ radical.

To put the calculation of $\langle n \rangle_3$ on the same basis as the above estimate for $\langle n \rangle_2$, we note that if ca. 55 free sites are distributed regularly on a surface with 221 regularly spaced sites, the separation of adjacent *free* sites is essentially twice the separation of adjacent headgroups. The latter distance is about 7 Å for the aggregates under study here,[3b] and hence the separation between adjacent free sites on the two-dimensional lattice is about 14 Å. Taking this distance as the length of one diffusional jump, we define our three-dimensional lattice to be one with lattice sites separated by $d = 14$ Å. Inasmuch as each lattice site may be regarded as occupying a volume $V \sim d^3$ in three-dimensional space, and given that each water molecule occupies a volume $v$, we determine that $N = V/v \sim 92$ water molecules are associated with each site in our three-dimensional lattice. Now, the total concentration of $Br_2^-$ produced in the experiment at time $t = 0$ in the 20 ns pulse is $2.69 \times 10^{-5}$ M. Since at this concentration of $Br_2^-$ we may safely use the approximation

$$X = (\mathrm{MW}/1000\rho)M$$

where $X$ and $M$ are the mole fraction and molarity of $Br_2^-$ and MW and $\rho$ are the molecular weight and density of the solvent, the trap concentration is given by

$$c = \frac{\text{no. of Br}_2^- \text{ radicals}}{\text{total no. of H}_2\text{O molecules}}\,\frac{\text{no. of H}_2\text{O molecules}}{\text{lattice site}}$$
$$= 4.44 \times 10^{-5} \text{ traps/total number of lattice sites}$$

Using Montroll's expression for $\langle n \rangle_3$, the prediction is that for a diffusion-controlled reaction in three-dimensional space, a minimum of $3.4 \times 10^4$ steps would be required on the average before the second $Br_2^-$ encounters the first $Br_2^-$ radical, and is subsequently trapped.

Given the estimates, $\langle n \rangle_3 \sim 3.4 \times 10^4$ steps vs. $\langle n \rangle_2 \sim 82$ steps, based on our use of Montroll's theory, it is of interest to construct the ratio $\langle n \rangle_2 / \langle n \rangle_3$ inasmuch as one expects this ratio to be in correspondence with the ratio of observed rate constants for intramicellar vs. intermicellar processes. The time for reactions of two $Br_2^-$ radicals in two- or three-dimension space is given by $\langle \tau \rangle_i = \langle n \rangle_i \cdot t_i$ where $t_i$ is the time required for a diffusional jump from one lattice point to the next and the subscript $i$ is the dimensionality. Assuming that the time and the distance between diffusional jumps is the same in both the two- and three-dimensional space (i.e., $d_2/v_2 = d_3/v_3$ and $d_2 = d_3$, where $d_i$ and $v_i$ are the distance between adjacent lattice sites and the hopping velocity), one obtains $\langle \tau \rangle_3 / \langle \tau \rangle_2 = \langle n \rangle_3 / \langle n \rangle_2$. This ratio can be related to the half-lifetimes of the dismutation reactions or, equivalently, the rate constants of the processes

$$\frac{k_2(\mathrm{a})}{2k_3(\mathrm{b}+\mathrm{c})} = \ln 2[\mathrm{Br}_2^-]_0 \frac{\langle n \rangle_3}{\langle n \rangle_2}$$

where labels a, b, and c refer to the pathways denoted in Figure 4. Inserting the values of $\langle n \rangle_3$ and $\langle n \rangle_2$ derived above and $[Br_2^-]_0 = 2.69 \times 10^{-5}$ M, we find that

$$k_2(\mathrm{a})/2k_3(\mathrm{b}+\mathrm{c}) = 7.7 \times 10^{-3}$$

which may be compared with the experimentally determined value.

$$k_2/2k_3 = 1.5 \times 10^{-3}$$

In light of the approximations involved in deriving the theoretical estimate, the agreement between the ratios is remarkably good. Less approximate calculations are now in progress to study further the effect of a reduction in dimensionality of reaction space on the kinetics of $Br_2^-$ radical reactions.

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(10) The referee suggested that $Br_2^-$ radicals located in a spherical shell within the diffuse layer may also contribute to the production of "intramicellar" $Br_3^-$. We believe, however, that the contribution of $Br_2^-$ in the diffuse layer is minor relative to that in the surface layer because of the large hydrophobicity of $Br_2^-$ referred to in the text and the steep gradient of the attractive electrical potential in the immediate vicinity of the micellar surface (ref 12c).

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