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Comparison of Reactivities of Dibromide Anion Radical and Dichloride Anion Radical in Neutral Aqueous Solution

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Synopsis. Rate constants of reactions of dibromide anion radical with some aliphatic dipeptides or unsaturated compounds including pyrimidine bases have been determined by flash photolysis. Difference in activation energy between dibromide and dichloride anion radicals has been estimated by comparing rate constants obtained for common substrates.

Dibromide anion radical ($\mathrm{Br_2}^{\overline{\cdot}}$ as well as dichloride anion radical ($\mathrm{Cl_2}^{\overline{\cdot}}$) has often been used as a probe for the oxidation of biomolecules.[1-6] The reactivities of both the anion radicals appear to be somewhat different from each other, in particular, with respect to specificity. No detailed investigation, however, has been found in literatures on the difference of their reactivities, because radiation-chemical determination of rate constants for $\mathrm{Cl_2}^{\overline{\cdot}}$ is restricted to acid solution. Recently, we found a convenient system to be used to determine rate constants for $\mathrm{Cl_2}^{\overline{\cdot}}$ in neutral aqueous solutions.[7-10] Thus, a quantitative comparison of reactivity between $\mathrm{Br_2}^{\overline{\cdot}}$ and $\mathrm{Cl_2}^{\overline{\cdot}}$ was attempted by determining rate constants for $\mathrm{Br_2}^{\overline{\cdot}}$ with some common substrates, with which rate constants had already been obtained for $\mathrm{Cl_2}^{\overline{\cdot}}$ in neutral aqueous solutions. Since at least two kinds of reactions, hydrogen atom abstraction and one-electron oxidation, are expected to take place with these anion radicals, a series of aliphatic dipeptides and some unsaturated compounds including several pyrimidine bases were adopted as common substrates. From the results obtained, some difference in activation energy could roughly be evaluated between $\mathrm{Br_2}^{\overline{\cdot}}$ and $\mathrm{Cl_2}^{\overline{\cdot}}$.

Experimental

Dipeptides were obtained from Nutritional Biochemical Corp. and pyrimidine bases from Sigma Chemical Corp. The other chemicals were of reagent grade.

Solutions for irradiation were prepared by dissolving 10^{-2} mol dm^{-3} KBr, 10^{-4} mol dm^{-3} $K_2S_2O_8$, and a desired amount of substrate in triply distilled water and adjusting pH to 7. The solutions were bubbled with N_2 for 20 min immediately before flash photolysis. Experimental conditions, the apparatus used for flash photolysis, and the procedure of kinetic analysis were described in detail elsewhere.[10,11]

Results and Discussion

During flash photolysis of N_2-saturated solutions containing 10^{-2} mol dm^{-3} KBr and 10^{-4} mol dm^{-3} $K_2S_2O_8$, the following reactions are expected to take place:

$$\mathrm{Br^-} + h\nu \longrightarrow \mathrm{Br}\cdot + e_{aq}^-, \tag{1}$$

$$\mathrm{S_2O_8}^{2-} + h\nu' \longrightarrow 2\mathrm{SO_4}^{\overline{\cdot}}, \tag{2}$$

$$e_{aq}^- + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{SO_4}^{\overline{\cdot}} + \mathrm{SO_4}^{2-}, \tag{3}$$

$$\mathrm{Br^-} + \mathrm{SO_4}^{\overline{\cdot}} \longrightarrow \mathrm{Br}\cdot + \mathrm{SO_4}^{2-}, \tag{4}$$

$$\mathrm{Br}\cdot + \mathrm{Br^-} \longrightarrow \mathrm{Br_2}^{\overline{\cdot}}. \tag{5}$$

Since the rate constant of Reaction 3 was reported to be 1.1×10^{10} dm^3 mol^{-1} s^{-1} and the concentration of $\mathrm{S_2O_8}^{2-}$ is 10^{-4} mol dm^{-3}, the lifetime of hydrated electrons is calculated as 9.1×10^{-7} s. If it is assumed that the rate constant k_4 is equal to that of the reaction of $\mathrm{SO_4}^{\overline{\cdot}}$ with $\mathrm{Cl^-}$, the lifetime $\mathrm{SO_4}^{\overline{\cdot}}$ with respect to Reaction 4 is 3.2×10^{-7} s. Therefore, the decay rate of $\mathrm{SO_4}^{\overline{\cdot}}$ due to Reaction 4 is faster than its formation by Reaction 3. Hence the lifetime of $\mathrm{SO_4}^{\overline{\cdot}}$ can be estimated to be of the order of 10^{-6} s. The lifetime with respect to Reaction 5 may be taken to be of the order of nanosecond because the rate constant of the analogous reaction, $\mathrm{Cl}\cdot+\mathrm{Cl^-}\rightarrow\mathrm{Cl_2}^{\overline{\cdot}}$, is known to be 2.1×10^{10} dm^3 mol^{-1} s^{-1}.[12] Since the rate constant of the reaction of $\mathrm{Br_2}^{\overline{\cdot}}$ with e_{aq}^- is 1.3×10^{10} dm^3 mol^{-1} s^{-1} [13] and $\mathrm{Br_2}^{\overline{\cdot}}$ of approximately 10^{-5} mol dm^{-3} has been observed to exist at the initial stage, a few percent portions of e_{aq}^- will be consumed by Reaction 6 in competition with Reaction 3:

$$e_{aq}^- + \mathrm{Br_2}^{\overline{\cdot}} \longrightarrow 2\mathrm{Br^-}. \tag{6}$$

The above discussion leads to a conclusion that the majority of reactive species found in the system 50 μs after start of flash are $\mathrm{Br_2}^{\overline{\cdot}}$. Since the kinetic analysis is based on the data obtained during the period 50—100 μs, the following reactions are conceivable to take place in the presence of substrate, S:

$$\mathrm{Br_2}^{\overline{\cdot}} + \mathrm{Br_2}^{\overline{\cdot}} \longrightarrow \mathrm{Br_2} + 2\mathrm{Br^-}, \tag{7}$$

$$\mathrm{Br_2}^{\overline{\cdot}} + \mathrm{S} \longrightarrow 2\mathrm{Br^-} + \text{product(s)}. \tag{8}$$

From these reactions a rate equation is derived as follows:

$$\ln\frac{[\mathrm{Br_2}^{\overline{\cdot}}]_0(2k[\mathrm{Br_2}^{\overline{\cdot}}]+k_{\mathrm{ob}})}{[\mathrm{Br_2}^{\overline{\cdot}}](2k[\mathrm{Br_2}^{\overline{\cdot}}]_0+k_{\mathrm{ob}})} - k_{\mathrm{ob}}t = 0, \tag{9}$$

where k_{ob} is equal to k_8 [S], $[\mathrm{Br_2}^{\overline{\cdot}}]_0$ and $[\mathrm{Br_2}^{\overline{\cdot}}]$ are the concentrations of $\mathrm{Br_2}^{\overline{\cdot}}$ at times zero and t, respectively, and $2k$ is the rate constant of Reaction 7. Equation 9 can be solved numerically for k_{ob} with the aid of microcomputer. The second order rate constant, k_8, is obtained by plotting k_{ob} vs. [S]. In Fig. 1, rate constants for $\mathrm{Cl_2}^{\overline{\cdot}}$ are plotted against those for $\mathrm{Br_2}^{\overline{\cdot}}$ for several aliphatic dipeptides, which are known to undergo hydrogen atom abstraction reaction with these anion radicals.[14] A linear relation can be seen between the reactivities of both the anion radicals, although there is left a small intercept, -6.4×10^6 dm^3 mol^{-1} s^{-1}. The slope is obtained as 9.9 with a correlation coefficient of 0.944. Similarly, a linear relation was found for some unsaturated compounds including pyrimidine bases, as shown in Fig. 2. A slope of 2.64 and an intercept of 2.9×10^7 dm^3 mol^{-1} s^{-1} are obtained with a correlation coefficient of 0.938. An addition

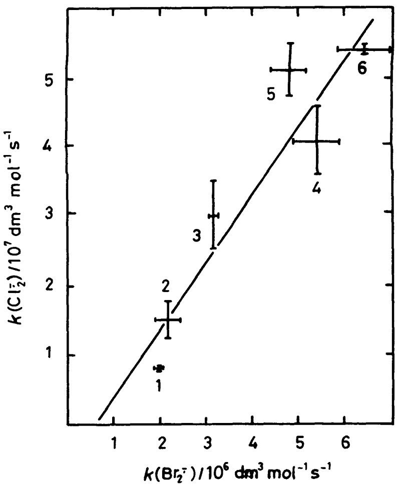

Fig. 1. $k(\mathrm{Cl}_2^{\cdot-})$ vs. $k(\mathrm{Br}_2^{\cdot-})$ for dipeptides.
1: Glycylglycine, 2: glycylalanine, 3: *N*-glycyl-2-aminobutyric acid, 4: glycylvaline, 5: glycylnorvaline, 6: glycylleucine. $k(\mathrm{Cl}_2^{\cdot-})$, see Ref. 7.

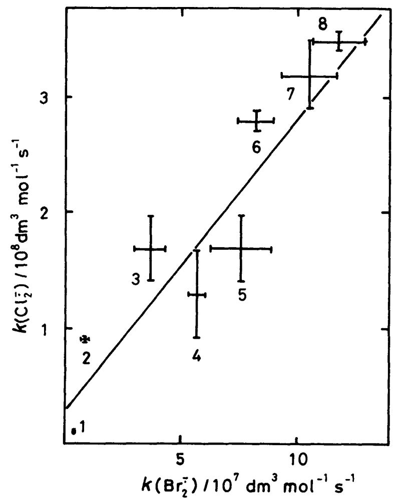

Fig. 2. $k(\mathrm{Cl}_2^{\cdot-})$ vs. $k(\mathrm{Br}_2^{\cdot-})$ for unsaturated compounds.
1: Pyrimidine, 2: acrylate, 3: maleate, 4: orotic acid, 5: isoorotic acid, 6: uracil, 7: thymine, 8: cytosine. $k(\mathrm{Cl}_2^{\cdot-})$, see Refs. 8 and 9.

reaction of $\mathrm{Cl}_2^{\cdot-}$ was reported for some unsaturated compounds.[14,15] If maleate and acrylate are excluded from the calculation, a slope of 3.1 and an intercept of $-2.1\times10^7\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ are obtained with a correlation coefficient of 0.968. Since ESR studies have shown that with pyrimidine bases one-electron oxidation takes place to yield their cation radicals,[16] the slope obtained above must correspond to the difference in reactivity of one-electron oxidation between $\mathrm{Br}_2^{\cdot-}$ and $\mathrm{Cl}_2^{\cdot-}$.

If the Arrhenius equation is applied, the apparent difference in activation energy between $\mathrm{Br}_2^{\cdot-}$ snd $\mathrm{Cl}_2^{\cdot-}$ for hydrogen atom abstraction or one-electron oxidation may be estimated from the slopes of the straight lines shown in Figs. 1 and 2, because each slope corresponds to a ratio of rate constants. For the estimation, the ratio of frequency factors is required. If the ratio is taken as unity, the differences in activation energy are 5.7 $\mathrm{kJ\,mol^{-1}}$ for hydrogen atom abstraction reaction and 2.4 $\mathrm{kJ\,mol^{-1}}$ for one-electron oxidation reaction. If the value 1.4, which is estimated from $2k$, is adopted as the ratio, they are 4.8 and 1.6 $\mathrm{kJ\,mol^{-1}}$ respectively. These values are smaller than the differences in heat of reaction obtainable from thermodynamic data, which satisfies the Horiuchi-Polanyi rule. Furthermore, these differences in activation energy indicate that $\mathrm{Br}_2^{\cdot-}$ is more appropriate to unsaturated compounds as a one-electron oxidation probe than $\mathrm{Cl}_2^{\cdot-}$.

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