Influence of Hexasulfonated Calix[6]arenes on the Reactivities of Arenediazonium Ions in an Aqueous System

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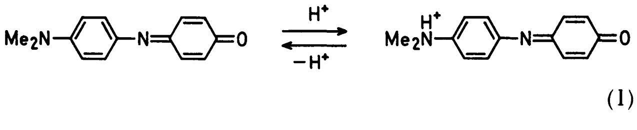
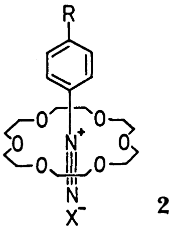
The pK_a of Phenol Blue shifted from 4.6 to 6.2 because of complexation of protonated Phenol Blue in the cavity of hexasulfonated calix[6]arene with dodecyl substituents (**2C$_{12}$**). The finding stimulated us to examine whether the analogs (**2C**) suppress the dediazoniation of arenediazonium ions in an aqueous system as crown ethers do in organic solvents. We have found that **2C** can suppress the dediazoniation in an aqueous system where neither 18-crown-6 nor anionic micelles are effective. The magnitude of the inhibition effect was 4—5 fold. The reaction rate of the diazo coupling with *N,N*-dimethylaniline was significantly suppressed in the presence of **2C**, suggesting that arenediazonium ions are deactivated through complexation with **2C**. The novel stabilization effects were explained by the strong anionic reaction field which neither 18-crown-6 nor anionic micelles have: that is, **2C** has a peculiar architecture that six sulfonato groups are circularly arranged on the edge of the calixarene cavity.

Recently, Gutsche and co-workers[1,2] have reported on a series of new cyclic molecules called "calixarenes" which are cyclic oligomers made up of benzene units as cyclodextrins are made up of glucose units. Several groups have reported on the ionophoric properties of calixarenes,[3–7] but almost nothing is known with certainty as to the inclusion properties of calixarenes in solution. In 1984, we reported the synthesis and properties of hexasulfonated calix[6]arenes, the first example of water-soluble calixarenes.[8] The subsequent investigations on these calixarenes established that they can form host-guest-type complexes with a variety of guest molecules in an aqueous system.[9–12] During these studies, we noticed an interesting spectral change in Phenol Blue: In the presence of hexasulfonated calix[6]arene (**2C$_{12}$**), the absorption maximum (658 nm in water) moves to 592 nm at low concentration region followed by a relatively small blue shift (630 nm) at high concentration region.[9] The λ_{max} 630 nm was equal to the blue shift induced by the sodium dodecyl sulfate(SDS) micelle,[9] but the origin of the unusually large blue shift to 592 nm was not explained until recently. We found, as described in this paper, that this blue shift is due to "protonation" of Phenol Blue in neutral aqueous solution (Eq. 1). The finding suggests that hexasulfonated calix[6]arenes, which have six anionic groups on the upper rim of the calixarene cavity, have some special architecture effecive to stabilize included cationic species.



(1)

In 1973, Gokel and Cram[13] found that crown ethers of the proper dimensions can solubilize several arenediazonium salts in nonpolar media (e.g., chloroform). Subsequent spectroscopic studies established that the solubilization is caused by complexation, like complexation between crown and metal cation, the linear Ar-N$^+$≡N inserting into the hole of the crown ring with its oxygen atoms turned inward toward the positive charge as shown in structure **1**.[13–19] As expected from the complex structure, the association constants (K) for crown-arenediazonium complexes are affected by both electronic effects and steric effects:[13–20] for example, strongly electron-donating groups (e.g, Et$_2$N-) in arenediazonium salts depress complexation to such extent that the K values cannot be determined[20] and the sterically hindered 2,6-dimethylbenzenediazonium salt is not complexed by crown ethers.[14] Of additional interest is the finding that the thermal decomposition of arenediazonium salts is slowed down when the salts are complexed by crown ethers.[17–19,21–23] This stabilization effect is attributed to the attenuation of the positive charge at the diazonium group in the complex[13,14,19] and to the retardation of the decomplexation rate.[23]



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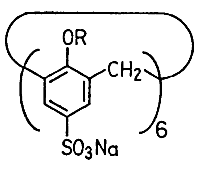
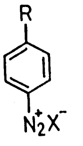


2C
2C$_1$: R=Me-
2C$_6$: R=Me(CH$_2$)$_5$-
2C$_{12}$: R=Me(CH$_2$)$_{11}$-



3R
3H: R=H-
3C$_6$: R=Me(CH$_2$)$_5$-
3Cl: R=Cl

Based on the foregoing results, we considered that **2C** may form stable complexes with arenediazonium salts (**3R**) and may stabilize them even in an aqueous system.[24] We here report that (i) the absorption maximum of Phenol Blue undergoes the unusual blue shift in the presence of **2C$_{12}$** due to electrostatic stabilization of protonated Phenol Blue, (ii) the dediazoniation of **3R** is significantly suppressed by complexation with **2C** even in an aqueous system where neither crown ethers nor anionic micelles are effective, and (iii) the rates of diazo coupling with *N,N*-dimethylaniline and 3-hydroxy-2,7-naphthalenedisulfonate (R-acid) are selectively slowed down.

Experimental

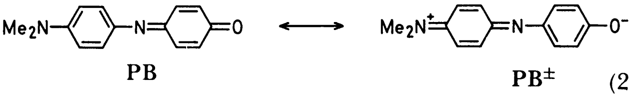
Materials. Preparations of 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexamethoxycalix[6]arene ($2C_1$), 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexakis(hexyloxy)calix[6]arene ($2C_6$), and 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexakis(dodecyloxy)calix[6]arene ($2C_{12}$) were described in a previous paper of this series.[9]

Kinetic Measurements. The rate constants for the dediazoniation were estimated as follows. Compound **3R** was prepard from aniline (or *p*-hexylaniline) by the reaction with $NaNO_2$ in 0.05 M† H_2SO_4 solution at 0—5 °C and then diluted with 0.024 M H_2SO_4 solution. This solution (containing $[\mathbf{3R}]=1.00\times10^{-3}$ M) was mixed with **2C** and maintained in the dark at 30 °C in a thermostated water bath. Aliquots were withdrawn from the reaction mixture and treated with 3-hydroxy-2,7-naphthalenedisulfonate in 0.10 M Na_2CO_3 solution. The concentration of unreacted **3R** was determined using a calibration curve by the absorption band (490 nm) of the diazo-coupling product. The plots of OD_{490} vs. reaction time were first-order for up to three half-lives.

The reaction between *p*-chlorobenzenediazonium ion **3Cl** and *N*,*N*-dimethylaniline (or 3-hydroxy-2,7-naphthalenedisulfonate) was followed spectrophotometrically at 30 °C. *p*-Chloroaniline was diazotized with $NaNO_2$ and diluted with an aqueous solution buffered to pH 6.92 (0.05 M phosphate) for *N*,*N*-dimethylaniline and to pH 4.80 (0.05 M acetate) for 3-hydroxy-2,7-naphthalenedisulfonate. This solution was equilibrated to 30 °C in a spectrophotometer and then mixed with 100 μl of aqueous *N*,*N*-dimethylaniline (or 3-hydroxy-2,7-naphthalenedisulfonate): [*p*-chlorobenzenediazonium ion]$=4.96\times10^{-5}$ M, [*N*,*N*-dimethylaniline]$=1.51\times10^{-3}$ M, [3-hydroxy-2,7-naphthalenedisulfonate]$=1.10\times10^{-3}$ M. The pseudo-first-order rate constants were estimated from the time-dependent appearence of a new absorption band for the product (440 nm for *N*,*N*-dimethylaniline and 490 nm for 3-hydroxy-2,7-naphthalenedisulfonate).

Results and Discussion

Absorption Spectra of Phenol Blue in the Presence of 2C. Brooker and Sprauge[25] suggested the use of Phenol Blue (PB) as a solvent property indicator; the absorption maximum (668 nm in water;[25] 658 nm according to our measurement at 30 °C) shifts to shorter wavelengths in nonpoler solvents e.g., 552 nm in cyclohexane). The blue shift is attributed to destabilization of the charge-separated excited state $PB^{\pm}$.



(2)

In the presence of $2C_{12}$ at pH 5.6 (no buffer), the λ_{max} of PB shifts to 592 nm at around $[2C_{12}]/[PB]\approx1$ and then moves to 630 nm at $[2C_{12}]/[PB]>1$ (Fig. 1). The absorption band at 592 nm is attributable to protonated species of PB, because (i) the similar absorption spectra (λ_{max} 570—590 nm) can be reproduced in acidic aqueous solution in the absence of $2C_{12}$ (Fig. 2) and (ii) the biphasic dependence of λ_{max} disappears in buffered aqueous solution (pH 8.7 with 0.02 M borate) (Fig. 1). This finding supports that protonated PB is strongly stabilized through inclusion in the cavity of $2C_{12}$. In Fig. 3, OD_{650} is plotted against pH. The solution pH was adjusted by HCl below pH 6 and aqueous NH_3 above pH 6. Thus, the pK_a of PB was estimated to be 4.6. In the presence of $2C_{12}$ the pK_a shifted to 6.2 (ΔpK_a=1.6), indicating that the included PB behaves as an apparently stronger base. The similar pK_a shift was also observed in the presence of the SDS micelle (pK_a=5.4; ΔpK_a=0.8), but the magnitude of the pK_a shift was about one-half.

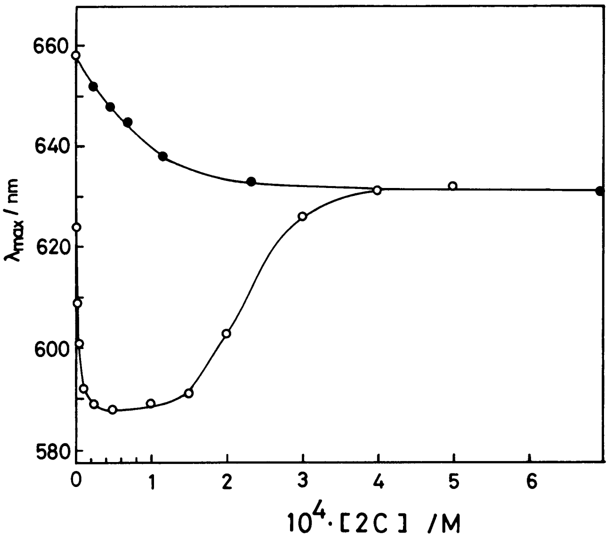


Fig. 1. Absorption maximum of Phenol Blue vs. $2C_{12}$ concentration: ○ at pH 5.6 (no buffer), ● at pH 8.7 with 0.02 M borate buffer. 30 °C, [Phenol Blue]$=1.00\times10^{-5}$ M.

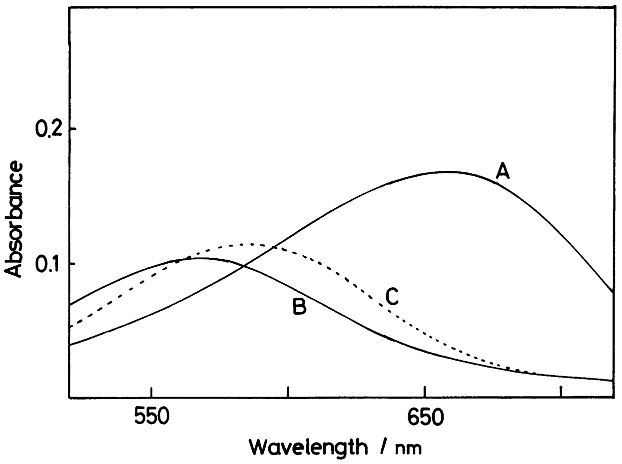


Fig. 2. Absorption spectra of Phenol Blue (1.00×10^{-5} M) at 30 °C: (A) pH 5.6 (no buffer), (B) pH 3.2 (with HCl), (C) pH 5.6 (no buffer, $[2C_{12}]=1.00\times10^{-4}$ M).

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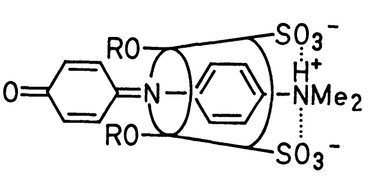
† 1 M=1 mol dm^{-3}.

The remarkable stabilization effect of $2C_{12}$ would be explained in two ways: That is, (i) oxonium ions are locally concentrated around $2C_{12}$ owing to the electrostatic interaction, resulting in a facile protonation of PB and (ii) hexa-anionic sulfonato groups stabilized the included, protonated PB through the host-guest-type electrostatic interaction. The effect (i) should be operative in the present system because addition of inorganic salts (e.g., NaCl) reduces the magnitude of the pK_a shift. This can be rationalized in terms of competitive binding of Na^+ and H_3O^+ to the anionic sulfonato groups. The effect (ii) should be also important. We have found that the "cone" conformation is favorably adopted when a guest molecule is included in the cavity of calixarenes.[26] When 2C adopts the cone conformation, six sulfonato groups are circularly arranged on one side of the calixarene cavity (Scheme 1). This unusual architecture would exert the remarkable stabilization effect on included cationic species. It is not easy to distinguish two effects on the basis of the present qualitative experiments. Probably, it is reasonable to consider that two effects are operative synergisticallly. If the effect (ii) contributes to the pK_a shift to a significant extent, one can extend this study to an interesting idea: That is, arenediazonium ions could be also stabilized through complexation with 2C.

Stabilization of Arenediazonium Ions. In the thermal decomposition of **3H**, we found by a GLC method that phenol is afforded in 58—65% yield as a sole detectable product in the absence and the presence of 2C([$2C_{12}$]=2.00 mM, 50 °C, 24 h). This indicates that the dediazoniation proceeds according to the ionic reaction path and the radical reaction path is not included.

The first-order rate constants (k_d) for the dediazoniation of **3H** and $3C_6$ are summarized in Table 1 and plots of k_d vs. [2C] for **3H** are illustrated in Fig. 4. Examination of Table 1 leads to the following conclusions: (i) in an aqueous system, neither 18-crown-6 nor anionic micelles suppress the thermal decomposition



Scheme 1.

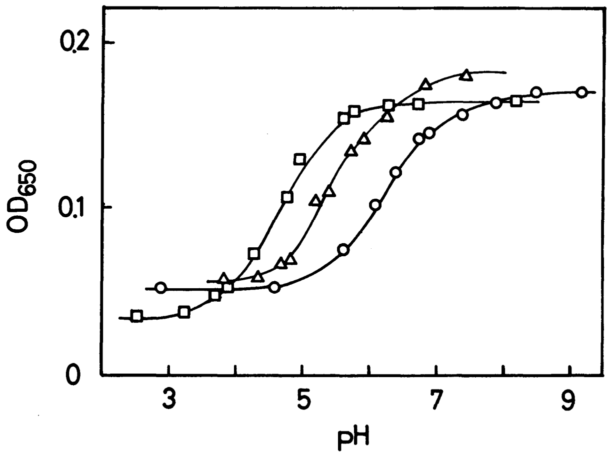


Fig. 3. pH-Dependence of the absorption band (650 nm) of Phenol Blue (1.00×10^{-5} M) at 30 °C: □ no additive, △ SDS (2.00×10^{-2} M), ○ $2C_{12}$ (1.00×10^{-5} M).

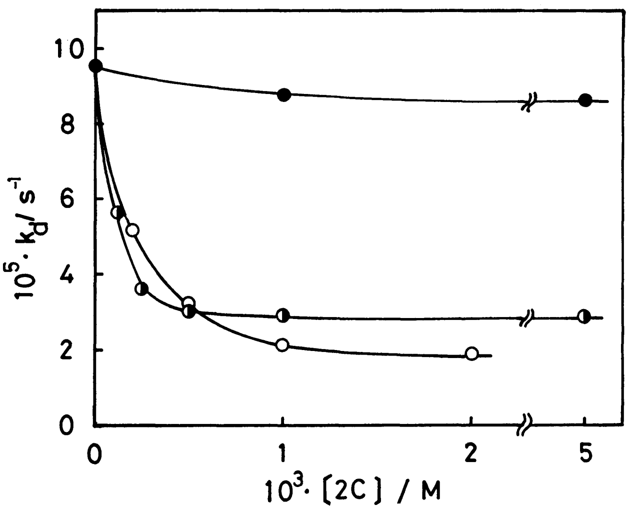


Fig. 4. Dediazoniation of **3H** (5.00×10^{-4} M) in the presence of 2C at 30 °C: ● $2C_1$, ◑ $2C_6$, ○ $2C_{12}$.

Table 1. First-Order Rate Constants (k_d) for Thermal Decomposition of Arenediazonium Salts (**3R**) at 30 °C

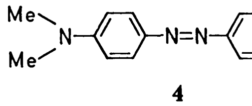
Additive (concn/mM)	3H		$3C_6$	
	$10^5 \cdot k_d/s^{-1}$	k_d/k_0	$10^5 \cdot k_d/s^{-1}$	k_d/k_0
None	9.52(=k_0)	1.00	1.60(=k_0)	1.00
$2C_1$ (5.00)	8.62	0.91	1.27	0.79
$2C_6$ (5.00)	2.92	0.31	0.37	0.23
$2C_{12}$ (2.00)	1.91	0.20	0.37	0.23
18-Crown-6 (24.4)	9.25	0.97	—	—
SDS[a] (20.0)	8.84	0.93	—	—
SDBS[b] (47.0)	8.72	0.92	—	—
Sodium *p*-toluenesulfonate (5.00)	9.46	0.99	—	—
Disodium 1,5-naphthalenedisulfonate (4.58)	9.60	1.01	—	—

a) Sodium dodecylsulfate: the cmc is 6.6 mM. b) Sodium dodecylbenzenesulfonate: the cmc is 1.2 mM.

of **3R** to a significant extent, (ii) 1,5-naphthalenedisulfonate, which is used as a stabilizer for arenediazonium salts in the solid state, is also ineffective, and (iii) the k_d values decrease with increasing concentration of **2C** and in particular, $\mathbf{2C_{12}}$ can reduce the k_d to 20—23% of those observed in the absence of **2C**. The fact (iii) is sharply contrastive to the fact (i) that 18-crown-6 can stabilize arenediazonium salts only in certain organic solvents but not at all in an aqueous system. These findings suggest that hexasulfonato calixarene derivatives have some specific architecture to stabilize **3R** even in an aqueous system. From the scheme depicted in Eq. 3, we estimated the association constans (K) and the intra-complex dediazoniation rate constants (k_{complex}) for 3H assuming the formation of a 1 : 1 complex:†† K=ca. 10^2 $\mathrm{M^{-1}}$ for $\mathbf{2C_1}$, 4.2×10^6 $\mathrm{M^{-1}}$ for $\mathbf{2C_6}$, and 5.6×10^4 $\mathrm{M^{-1}}$ for $\mathbf{2C_{12}}$; $k_{\mathrm{complex}}=8.62\times10^{-5}$ $\mathrm{s^{-1}}$ for $\mathbf{2C_1}$, 2.92×10^{-5} $\mathrm{s^{-1}}$ for $\mathbf{2C_6}$, and 1.91×10^{-5} $\mathrm{s^{-1}}$ for $\mathbf{2C_{12}}$. These results support that hexa-anionic **2C** can form stable complexes with cationic **3H**. Since the K values for $\mathbf{2C_6}$ and $\mathbf{2C_{12}}$ are much greater than that for $\mathbf{2C_1}$, not only the electrostatic interaction but also the hydrophobic force is operative in the association with **3H**. We previously found that $\mathbf{2C_6}$ forms micelle-like aggregates, the cmc being detected at 0.6 mM while $\mathbf{2C_{12}}$ acts as a "unimolecular" micelle at 10^{-5}—10^{-3} M region forming host-guest type 1 : 1 complexes with guest molecules.[9] The fact that the K for $\mathbf{2C_6}$ is greater by a factor of 75 than that for $\mathbf{2C_{12}}$ may be due to the aggregate formation of $\mathbf{2C_6}$.

$$\begin{tikzcd}
\mathrm{3H} + \mathrm{2C} \arrow[r, shift left, "K"] \arrow[d, "k_0(=9.52\times10^{-5}\mathrm{s^{-1}})"] & \mathrm{3H\cdot2C} \arrow[l, shift left] \arrow[d, "k_{\mathrm{complex}}"] \\
\text{product} & \text{product}
\end{tikzcd} \tag{3}$$

To obtain an insight into the binding mode of **3R** into the calixarene cavity, we examined the solvent effect on the dediazoniation rate because the hydrophobic effect in an aqueous system is partly reproduced by the solvent effect. We used 4-(4-dimethylaminophenylazo)benzenediazonium tetrafluoroborate (**4**) as a spectroscopic probe. The absorption maximum of **4** shifts to shorter wavelengths in nonpolar solvents: For example, λ_{max} 612 nm in water, 579 nm in tetrahydrofuran, and 558 nm in dioxane (30 °C). In Fig. 5, the λ_{max} is plotted against the dioxane concentration in water. The λ_{max} shifts to shorter wavelengths with increase in the dioxane concentration. In an aqueous system, the λ_{max} was not affected by the addition of $\mathbf{2C_1}$ (2.00 mM) but shifted to 609 and 595 nm in the presence of $\mathbf{2C_6}$ and $\mathbf{2C_{12}}$ (2.00 mM), respectively. These wavelenghts correspond to the aqueous solutions containing 25 and 85 vol% of dioxane. This implies that **3R** is bound to the relatively hydrophobic site in the calixarene cavity.



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In Fig. 6, the k_d values are plotted against the λ_{max} of **4**. The open circles indicate the rate constants obtained for **3H** in an aqueous system in the presence of additives, and the filled circles indicate the rate constants obtained for benzenediazonium tetrafluoroborate in a dioxane-water system. It is seen from Fig. 6 that the plots for most additives are not so different from those for a dioxane-water system, but two plots

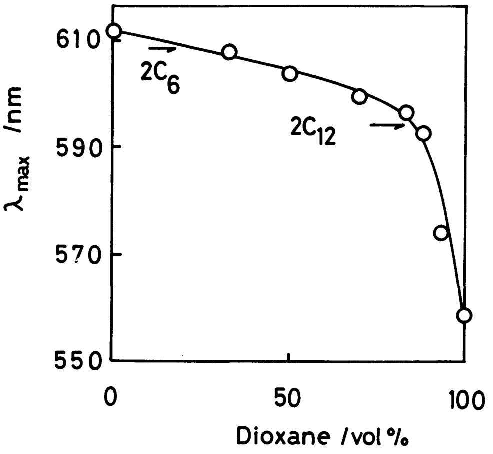

Fig. 5. Absorption maximum of **4** (1.78×10^{-5} M) in water–dioxane at 30 °C. The arrows indicate the "hydrophobicity" of **2C** in an aqueous system.

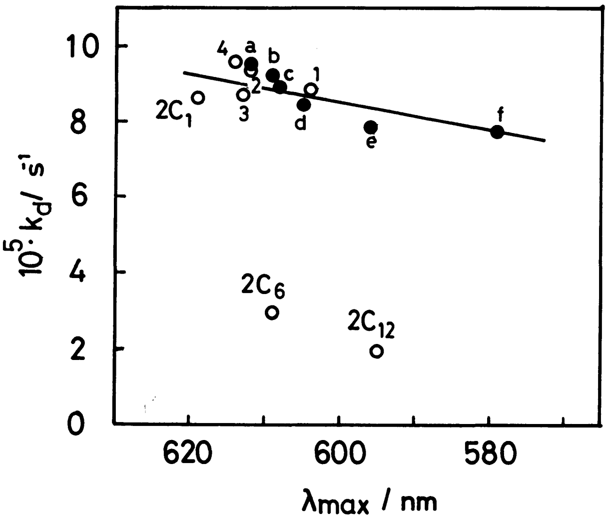

Fig. 6. First-order rate constant for the dediazoniation of **3H** vs. absorption maximum of **4** (the longer the wavelength, the more hydrophobic): (1) SDS (2.00×10^{-2} M), (2) sodium *p*-toluenesulfonate (5.00×10^{-3} M), (3) sodium dodecylbenzenesufonate (4.70×10^{-2} M), (4) disodium naphthalene-1,5-disulfonate (4.58×10^{-3} M). (a)—(f) indicate a water–dioxane system; the dioxane concentrations (vol%) are (a) 0, (b) 25, (c) 33, (d) 49, (e) 82, (f) 93.

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††The detailed calculation method equivalent to Eq. 3 was described previously: S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **105**, 1851 (1983).

for $2C_6$ and $2C_{12}$ are distinctly deviated from this relationship. This implies that the stabilization effect of $2C_6$ and $2C_{12}$ is not fully explained by the hydrophobic effect. We believe that the specific stabilization is due to the strong anionic field brought about by six sulfonato groups on the edge of the calixarene cavity. Therefore, the hexasulfonated calix[6]arene has an architecture very favorable to stabilize the complexed arenediazonium ions.

Influence on the Diazo-Coupling Reactions. The decomposition of arenediazonium ions is efficiently suppressed through complexation with hexasulfonated calix[6]arenes. As a next stage, it is of a great significance to examine the reactivity of these stabilized arenediazonium ions in the diazo-coupling reactions. However, this seems fairly difficult because in contrast to the unimolecular dediazoniation the rate of the bimolecular diazo-coupling reaction reflects not only the reactivity of arenediazonium ions but also the local concentration effect. We chose the reaction with neutral species, *N*,*N*-dimethylaniline (DA) in order to obviate at least the complexity arising from the electrostatic interaction and repulsion between charged reactants. As **3H** and $\mathbf{3C_6}$ did not exhibit a measurable reactivity toward DA, we employed more reactive arenediazonium ion, *p*-chlorobenzenediazonium (**3Cl**).

First, we tested whether the dediazoniation of **3Cl** is really suppressed by **2C**. The reaction was carried out at 60 °C because **3Cl** decomposed very slowly at 30 °C. As shown in Fig. 7, this reaction is also slowed down in the presence of $2C_6$ and $2C_{12}$: K=5.0×10^4 M and k_d/k_0=0.18 for $2C_6$ (2.00 mM) and K=5.2×10^4 M and k_d/k_0=0.30 for $2C_{12}$ (2.50 mM). In Fig. 8, the pseudo-first-order rate constants (k_c) for the diazo-coupling reaction at 30 °C are plotted against the calixarene concentrations. The k_c for sodium dodecyl sulfate (SDS; the cmc is 6.6 mM) sharply increased at 0—7 mM region and then decreased at higher concentration region. The biphasic dependence can be explained by the micellar effect on the bimolecular reaction:[27] The rate acceleration at the low concentration region would be due to the formation of a hydrophobic ion pair[27,28] between **3Cl** and SDS leading to the enhancement in the local concentration, whereas the rate retardation at the high concentration region would be due to the so-called dilution effect caused by the micellar aggregates.[27] The effect of added **2C** is quite contrasting: $2C_6$ and $2C_{12}$ which strongly associated with arenediazonium ions decelerated the reaction monotonously, while $2C_1$, which associated with arenediazonium ions only weakly accelerated the reaction to some extent. The typical rate constants are summarized in Table 2.

Probably, one has to take two different effects into consideration to account for the kinetic results in Fig. 8. The first is the stabilization of **3Cl** through complexation with **2C**, leading to the rate retardation. The second effect is the concentration of reactants in the calixarene cavity, leading to the rate acceleration as seen for the SDS system. As shown in Fig. 8 and Table 2, the k_c values were decreased by 11—13 fold in the presence of $2C_6$ and $2C_{12}$ in spite of the expected, positive contribution of the concentration effect. This suggests that arenediazonium ions included in the calixarene cavity are considerably deactivated. However, it is also possible to explain the kinetic data in a different way on the basis of the concentration effect: For example, possible explanations are (i) the cavity of **2C** can accept only one guest molecule and therefore

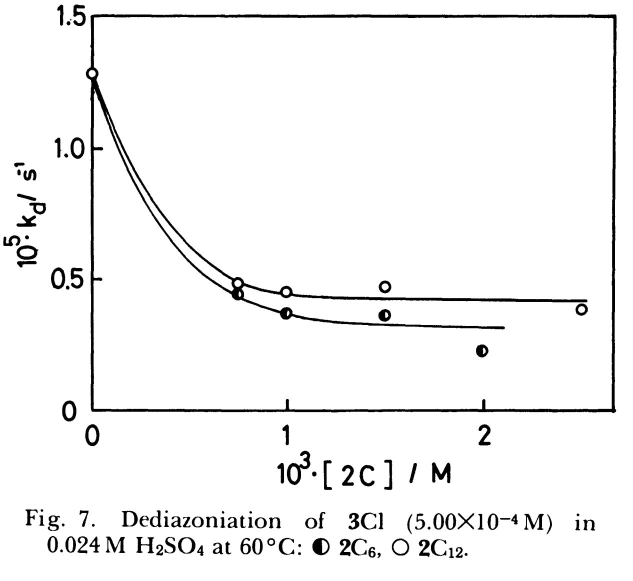

Fig. 7. Dediazoniation of **3Cl** (5.00×10^{-4} M) in 0.024 M H_2SO_4 at 60 °C: ◐ $2C_6$, ○ $2C_{12}$.

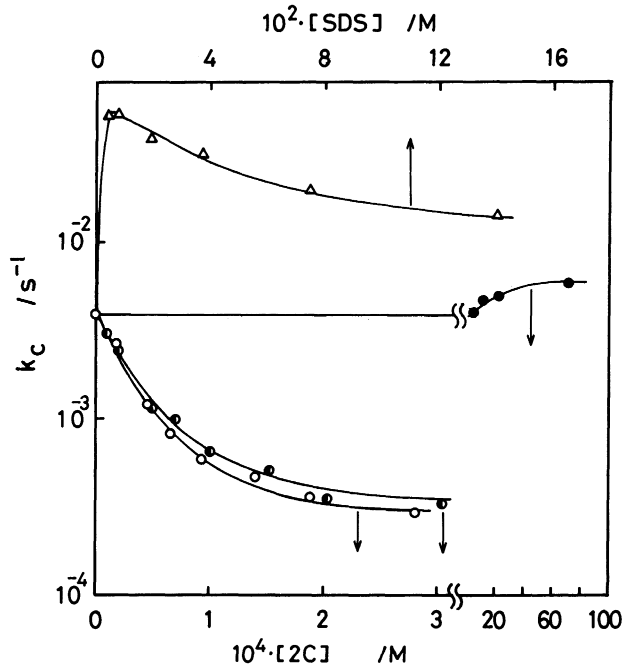

Fig. 8. Semi-log plots for diazo coupling of **3Cl** (4.96×10^{-5} M) with *N*,*N*-dimethylaniline (1.51×10^{-3} M) at 30 °C and pH 6.92 with 0.05 M phosphate buffer. ● $2C_1$, ◐ $2C_6$, ○ $2C_{12}$, △ SDS.

Table 2. Pseudo-First-Order Rate Constants (k_c) for the Diazo-Couping Reactions at 30 °C

Calixarene (concn/mM)	N,N-Dimethylaniline		3-Hydroxy-2,7-naphthalenedisulfonate	
	$10^3 \cdot k_c/s^{-1}$	k_c/k_0	$10^4 \cdot k_c/s^{-1}$	k_c/k_0
None	3.86 (=k_0)	1.00	3.56 (=k_0)	1.00
$2C_1$ (7.04)	5.90	1.53	2.15	0.60
$2C_6$ (0.271)	0.350	0.091	0.087	0.024
$2C_{12}$ (0.297)	0.297	0.077	0.058	0.016
SDS (7.51)	52.7	14	0.715	0.20
SDS (108)	15.9	4.12	0.070	0.020

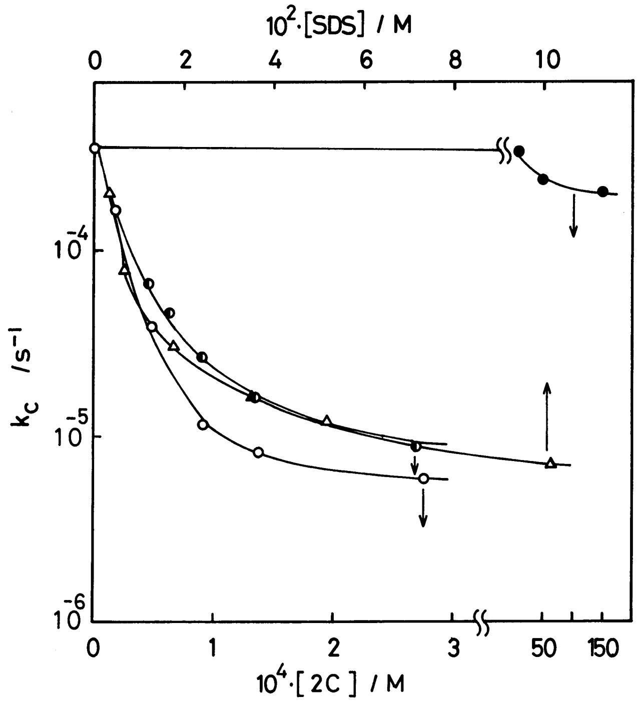

Fig. 9. Semi-log plots for diazo coupling of **3**Cl (4.96×10^{-5} M) with 3-hydroxy-2,7-naphthalenedisulfonate (1.10×10^{-3} M) at 30 °C and pH 4.80 with 0.05 M acetate buffer. ● $2C_1$, ◐ $2C_6$, ○ $2C_{12}$, △ SDS.

retards the rate of the bimolecular diazo coupling and (ii) **2C** has two binding sites, one consisting of sulfonated benzene rings suitable to bind a cationic guest molecule (e.g., **3**Cl) and the other consisting of alkyl (hexyl or dodecyl) groups suitable to bind a neutral guest molecule (e.g., DA). In either case, the reaciton rate should be suppressed by the apparent dilution of reactants. In particular, the case (ii) is likely because $2C_1$, in which the binding site consisting of alkyl (methyl) groups is relatively weak accelerates the reaction rate (Fig. 8). At present we believe that the efficient rate retardation results from both the deactivation of **3**Cl and the dilution of **3**Cl and DA.

The effect of added **2C** may be shown more clearly by the combination with the electrostatic repulsion. This combination may be of some significance because the diazo-coupling reaction usually includes the attack of cationic arenediazonium ions at anionic species (e.g., phenolate anion). We chose 3-hydroxy-2,7-naphthalenedisulfonate (pK_a 9.42 under the present reaction conditions). The kinetic results are illustrated in Fig. 9. We found that the reaction is strongly inhibited by $2C_6$ and $2C_{12}$, the rate constants being smaller by 42—63 fold than that in a non-additive system (Table 2). A similar rate retardation was observed for SDS, the inhibition effect (50 fold) being comparable with that for $2C_6$ and $2C_{12}$. One can thus envisage a reaction mode such **3**Cl is bound to the anionic calixarene or to the SDS micelle by the electrostatic interaction and 3-hydroxy-2,7-naphthalenedisulfonate is separated by the electrostatic repulsion. Since the inhibition effect is comparable between **2C** and SDS, this reaction should be primarily governed by the electrostatic effect and the stabilization of **3**Cl by **2C** should play only a secondary role. It is worthy mentioning, however, that $2C_6$ and $2C_{12}$ sufficiently inhibit the reaction at 10^{-4} M region while the same inhibition is attained by 10^{-2} M SDS. This implies that the electrostatic effect of **2C** is much superior to that of the SDS micelle.

Conclusion

The present study demonstrated that hexasulfonated calixarene can provide a very strong anionic environment which is effective to suppress the dediazoniation and the diazo coupling. The novel behaviors arise from the peculiar architecture of **2C** which has six anionic charges on the upper rim of the calixarene cavity. Further applications to host molecules, catalysts, etc. are now continued in this laboratory.

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