Stabilization of Arenediazonium Ions by Complexation with Hexasulphonated Calix[6]arenes in an Aqueous System

Seiji Shinkai,* Seiichi Mori, Takashi Arimura, and Osamu Manabe

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

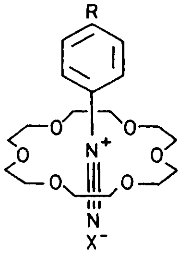
Hexasulphonated calix[6]arenes (**2b**) and (**2c**) can suppress the dediazoniation of arenediazonium salts in an aqueous system where neither 18-crown-6 nor anionic micelles are effective.

In 1973, Gokel and Cram[1] found that crown ethers of suitable dimensions can solubilize several arenediazonium salts in non-polar media (*e.g.*, chloroform). Subsequent spectroscopic studies established that the solubilization is caused by complexation, the linear Ar–N$^+$≡N inserting into the cavity of the crown ring with its oxygen atoms turned in towards the positive charge as shown in structure (**1**).[1—7] As expected from the complex structure, the association constants (*K*) for crown–arenediazonium complexes are affected by both electronic effects and steric effects:[1—8] for example, strongly electron-donating groups (*e.g.*, Et_2N–) in arenediazonium salts depress complexation to such an extent that the *K* values cannot be determined[8] and the sterically hindered 2,6-dimethylbenzenediazonium salt is not complexed by crown ethers.[2] Of additional interest is the finding that the thermal decomposition of arenediazonium salts is slowed when the salts are complexed by crown ethers.[5—7,9—11] This stabilization of arenediazonium salts is attributed to the reduction of

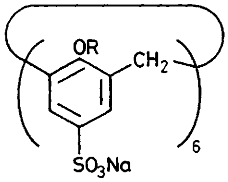
Table 1. First-order rate constants (*k*) for thermal decomposition of arenediazonium salts (**3**) at 30 °C.

Additive	Conc./ mM	(**3a**) $10^5 \cdot k$/s^{-1}	(**3a**) k/k_0	(**3b**) $10^5 \cdot k$/s^{-1}	(**3b**) k/k_0
None		9.52	1.00	1.60	1.00
(**2a**)	5.0	8.62	0.91	1.27	0.79
(**2b**)	5.0	2.92	0.31	0.37	0.23
(**2c**)	2.0	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 toluene-*p*-sulphonate	5.0	9.46	0.99	—	—
Disodium naphthalene-1,5-disulphonate	4.58	9.60	1.01	—	—

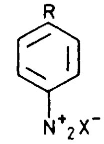
[a] Sodium dodecylsulphate; the critical micelle concentration (c.m.c.) is 6.6 mM. [b] Sodium dodecylbenzenesulphonate; the c.m.c. is 1.2 mM.



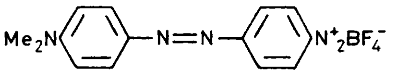
(1)



(2) **a**; R = Me
b; R = n-hexyl
c; R = n-dodecyl



(3) **a**; R = H
b; R = n-hexyl



(4)

the positive charge at the diazo group in the complex[1,2,7] and to the retardation of the decomplexation rate.[11]

Recently, we synthesized water-soluble calix[6]arene derivatives (**2**), in which six sulphonate groups and six alkyl groups are attached at the two sides of the calix[6]arene cavity.[12—14] We found that (**2**) can provide an anionic reaction medium much stronger than anionic micelles, poly(styrene-*p*-sulphonate), *etc.*[12,13] It occurred to us, therefore, that the six sulphonate groups may be capable of stabilizing arenediazonium salts (**3**) in an aqueous system if they are bound at certain positions in the calixarene cavity. We here report that in the presence of (**2**) the dediazoniation of (**3**) is significantly suppressed even in an aqueous system where neither crown ethers nor anionic micelles are effective.

Compound (**3**) was prepared from aniline (or *p*-n-hexylaniline) by 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 $\{[(\mathbf{3})] = 1.00 \times 10^{-3}\,\text{M}\}$ was mixed with (**2**) and maintained in the dark at 30 °C in a thermostatted water-bath.† Aliquots were withdrawn from the reaction mixture and treated with 2-hydroxynaphthalene-3,6-disulphonate (*i.e.*, R-acid) in 0.10 M Na_2CO_3 solution. The concentration of unreacted (**3**) was determined (using a calibration curve) from the intensity of the absorption band (490 nm) of the azo-coupling product. The plots of the optical density at 490 nm *vs.* reaction time were first-order. Typical first-order rate constants (k) thus determined are summarized in Table 1, and plots of k *vs.* [(**2**)] for the reaction with (**3a**) are illustrated in Figure 1(a).

The data in Table 1 lead to the following conclusions concerning the aqueous system: (i) neither 18-crown-6 nor anionic micelles suppress the thermal decomposition of (**3**) to a significant extent; (ii) naphthalene-1,5-disulphonate, which is used as a stabilizer for arenediazonium salts in the solid state, is also ineffective; (iii) the k values decrease with increasing concentration of (**2**) and in particular, (**2c**) can reduce k to 20—23% of those observed in the absence of (**2**).

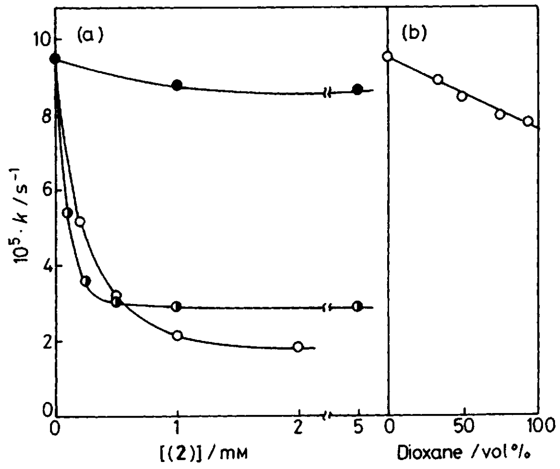


Figure 1. (a) Dediazoniation of (**3a**) (5.00×10^{-4} M) in the presence of (**2**) at 30 °C. ● (**2a**); ◑ (**2b**); ○ (**2c**). (b) Dediazoniation of benzenediazonium tetrafluoroborate (1.78×10^{-5} M) in water–dioxane at 30 °C.

This last point sharply contrasts with the fact 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 hexasulphonate calixarene derivatives have some specific architecture which can help to stabilize (**3**) even in an aqueous system. From equation (1) the association constants (K) and the intra-complex dediazoniation rate constants (k_{complex}) for (**3a**) assuming the formation of a 1 : 1 complex were estimated as: $K = ca.\ 10^2$ mol^{-1} dm^3 for (**2a**), 4.2×10^6 mol^{-1} dm^3 for (**2b**), and 5.6×10^4 mol^{-1} dm^3 for (**2c**); $k_{\text{complex}} = 8.62 \times 10^{-5}$ s^{-1} for (**2a**), 2.92×10^{-5} s^{-1} for (**2b**), and 1.91×10^{-5} s^{-1} for (**2c**).‡

$$\begin{tikzcd} (\mathbf{3a}) + (\mathbf{2}) \arrow[r, shift left, "K"] \arrow[d, "k_0\ (= 9.52 \times 10^{-5}\ \text{S}^{-1})"] & (\mathbf{3a})\text{–}(\mathbf{2}) \arrow[l, shift left] \arrow[d, "k_{\text{complex}}"] \\ \text{Product} & \text{Product} \end{tikzcd} \tag{1}$$

To obtain an insight into the binding mode of (**3**) in the calixarene cavity, we synthesized 4-(4′-dimethylaminophenylazo)benzenediazonium tetrafluoroborate (**4**) as a spectroscopic probe. The absorption maximum of (**4**) (612 nm in water) shifts to shorter wavelengths in non-polar solvents: for example, $\lambda_{\text{max.}}$ 579 nm in tetrahydrofuran and 558 nm in dioxane (30 °C). In an aqueous system, the $\lambda_{\text{max.}}$ was not affected by the addition of (**2a**) (2.00 mM) but shifted to 609 and 595 nm in the presence of (**2b**) and (**2c**) (2.00 mM), respectively. These wavelengths correspond to the aqueous solutions containing 25 and 85 vol% of dioxane. This implies that (**3**) is bound to the relatively hydrophobic site in the calixarene cavity.

The effect of hydrophobicity on the dediazoniation can be reproduced by the solvent effect. We determined the k for the dediazoniation of benzenediazonium tetrafluoroborate in water–dioxane mixed solvents by monitoring the disappearance of the absorption band (260 nm) spectrophotometrically.

---

† In the thermal decomposition of (**3a**), phenol was afforded in 58—65% yield as the sole detectable product in the absence and the presence of (**2**) $\{[(\mathbf{2c})] = 2.00$ mM, 50 °C, 24 h$\}$. This indicates that the dediazoniation proceeds *via* an ionic reaction path and not a radical reaction path.

‡ We previously found that (**2b**) forms micelle-like aggregates, the critical micelle concentration (c.m.c.) being 0.6 mM, while (**2c**) acts as a 'unimolecular' micelle forming host–guest-type 1 : 1 complexes with guest molecules.[12] The fact that K for (**2b**) is greater by a factor of 75 than that for (**2c**) may be due to the aggregate formation of (**2b**).

As illustrated in Figure 1(b), the value of k decreased with increasing dioxane concentration, but the change was relatively small ($k_{93\%\ \text{dioxane}}/k_{\text{water}} = 0.81$). This indicates that even though (**3**) is bound to the hydrophobic site in the calixarene cavity, the stabilization effect of (**2**) cannot be fully rationalized in terms of the hydrophobic effect. Conceivably, the stabilization is explained by the strong anionic reaction medium which neither 18-crown-6 nor anionic micelles have: that is, (**2b**) and (**2c**) have six sulphonate groups on one side of the calixarene cavity. The very strong anionic environment arising from this architecture could be the origin of the stabilization of the arenediazonium salts in an aqueous system.

This research was supported in part by a grant from the Ministry of Education of Japan.

Received, 17th October 1986; Com. 1481

References

1 G. W. Gokel and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 1973, 482.
2 E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel. T. L. Tarnowski, S. S. Moore, and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 2564.
3 B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, 1975, **14**, 541.
4 S. H. Korzeniowski, R. J. Petcavich, M. M. Coleman, and G. W. Gokel, *Tetrahedron Lett.*, 1977, 2647; J. R. Beadle, R. K. Khanna, and G. W. Gokel, *J. Org. Chem.*, 1983, **48**, 1242.
5 R. A. Bartsch, H. Chen, N. F. Haddock, and P. N. Juri, *J. Am. Chem. Soc.*, 1976, **98**, 6753.
6 R. A. Bartsch and P. N. Juri, *J. Org. Chem.*, 1980, **45**, 1011.
7 G. W. Gokel, S. H. Korzeniowski, and L. Blum, *Tetrahedron Lett.*, 1977, 1633; S. H. Korzeniowski and G. W. Gokel, *ibid.*, 1977, 1637.
8 R. M. Izatt, J. D. Lamb, B. E. Rossiter, N. E. Izatt, and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 1978, 386; R. M. Izatt, J. D. Lamb, C. S. Swain, J. J. Christensen, and B. L. Haymore, *J. Am. Chem. Soc.*, 1980, **102**, 3032.
9 P. N. Juri and R. A. Bartsch, *J. Org. Chem.*, 1979, **44**, 143.
10 J. R. Beadle and G. W. Gokel, *Tetrahedron Lett.*, 1984, **25**, 1681.
11 H. Nakazumi, I. Szele, K. Yoshida, and H. Zollinger, *Helv. Chim. Acta*, 1983, **66**, 1721.
12 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, and O. Manabe, *J. Am. Chem. Soc.*, 1986, **108**, 2409.
13 S. Shinkai, H. Koreishi, S. Mori, T. Sone, and O. Manabe, *Chem. Lett.*, 1985, 1033.
14 For comprehensive reviews on calixarenes see C. D. Gutsche, *Acc. Chem. Res.*, 1983, **16**, 161; C. D. Gutsche, 'Host Guest Complex Chemistry/Macrocycles,' Springer-Verlag, Berlin, 1985, p. 375.