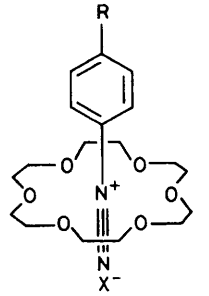
Can Calixarene Esters Stabilise Arenediazonium Ions by Complexation?

Seiji Shinkai,* Sayuri Edamitsu, Takashi Arimura, and Osama Manabe

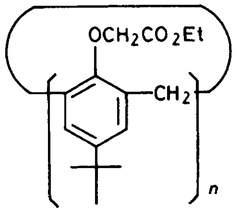
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

Calix[6]arene ester (**2**; $n = 6$) strongly binds arenediazonium ions as do crown ethers but does not inhibit dediazoniation; showing that its inhibition by crown ethers is caused by steric effects and not reduction of the positive charge at the diazo group.

In 1973, Gokel and Cram[1] found that crown ethers of appropriate dimensions can solubilise several arenediazonium salts in nonpolar solvents (*e.g.*, chloroform). Subsequent spectroscopic studies established that solubilisation is achieved by complexation, the linear $Ar{-}N^+{\equiv}N$ inserting into the cavity of the crown ring with its oxygen atoms turned towards the positive charge as shown in structure (**1**).[1—5] The thermal decomposition of arenediazonium salts is slower when the salts are complexed by crown ethers,[4—8] but the stabilisation mechanism is still uncertain. Two opposing



(1)



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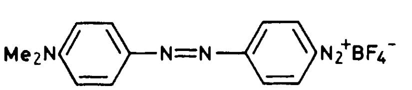

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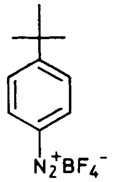

(4)

A

Table 1. Absorption maxima and association constants for (3).[a]

Host molecule	λ_{max}/nm	$\Delta\lambda^b$/nm	K/ $mol^{-1} dm^3$
None	680(= λ_0)		
Monobenzo-15-crown-5	648	32	230
18-Crown-6	565	115	178 000
1,17-Dichloro-3,6,9,12,15-pentaoxaheptadecane	625	55	450
(2; n = 4)	659	21	96
(2; n = 6)	557	123	16 500
(2; n = 8)	637	43	210

[a] 40 °C, tetrachloroethane, [host]/[(3)] = 10, [(3)] = 3.00 × 10^{-5} M.
[b] $\Delta\lambda = \lambda_0 - \lambda_{max}$.

mechanisms have been proposed: that is, the thermal decomposition is suppressed because of (i) reduction of the positive charge at the diazo group through interaction with oxygen lone pairs, or (ii) the macrocyclic effect, which sterically inhibits dediazoniation proceeding from the linear Ar–$N^+\equiv N$ inserted in the crown ring to the bulky π-intermediate **A**.[7]

More recently, several groups found that calixarene esters (**2**) also complex alkali metal cations.[9—11] To investigate whether arenediazonium salts are also complexed and stabilised by (**2**), we used 4′-dimethylaminoazobenzene-4-diazonium tetrafluoroborate (**3**) which serves as a spectroscopic probe.[12] Compound (**3**) has push–pull-type substituents which cause an intramolecular charge-transfer band, so that the absorption maximum should reflect sensitively the reduction of the positive charge at the diazo group.[12] The absorption maximum of (**3**) (680 nm in tetrachloroethane) shifted to shorter wavelengths with several isosbestic points with increasing (**2**) concentrations. A similar trend was observed for monobenzo-15-crown-5 and 18-crown-6. This blue shift implies that intramolecular charge-transfer is suppressed because of the reduction of the positive charge at the diazo group. The continuous variation plots support the theory that these additives all form 1:1 complexes with (**3**). We thus determined the association constants (K) from plots of the absorbance at 680 nm *vs.* additive concentrations. The results are summarised in Table 1.

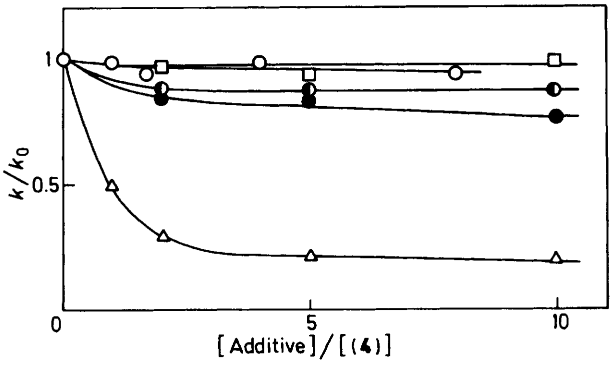

Figure 1. Dediazoniation of (4) (1.00 × 10^{-4} M) in the presence of crown ethers and (2) in tetrachloroethane at 40 °C. □, Monobenzo-15-crown-5; ○, (2; n = 4); ◐, (2; n = 6); ●, (2; n = 8); △, 18-crown-6.

18-Crown-6 and (**2**; n = 6) cause the largest blue shifts (115—123 nm) and the resultant K values are greater than 10^4 $mol^{-1} dm^3$, supporting the idea that (**2**; n = 6) strongly complexes the diazo group, the interaction being comparable with that with 18-crown-6. In contrast, monobenzo-15-crown-5 and (**2**; n = 4) cause a blue shift of only 21—32 nm and the K values are relatively small (96—230 $mol^{-1} dm^3$). According to previous reports on the ion selectivity, (**2**; n = 4) binds Na^+ selectively, while (**2**; n = 6) is more selective towards K^+.[9—11] Thus, the K^+-selective ionophores can associate strongly with the diazo group but the Na^+-selective ionophores cannot. Similarly, both the blue shift and the K value for (**2**; n = 8) are small. The cavity is too large to be accommodated with the diazo group, and the low affinity of (**2**; n = 8) for K^+ has been observed previously.[9—11]

The dediazoniation rate of *p*-t-butylbenzenediazonium tetrafluoroborate (**4**) was measured in the presence of these additives (Figure 1) by monitoring the disappearance of the absorption band at 284 nm. As reported previously,[4—8] 18-crown-6 suppressed the rate efficiently, whereas inhibition was scarcely observed for monobenzo-15-crown-5. The kinetic data for the crown ether family are corroborate to the spectral data in Table 1. The reaction was scarcely or only slightly suppressed by (**2**) [including (**2**; n = 6)]: the inhibition effect decreased in the order (**2**; n = 8) > (**2**; n = 6) > (**2**; n = 4). The lack of inhibition indicates that reduction of the positive charge, *i.e.* mechanism (i), is not responsible for the stabilisation of the diazo group.

It is known that, although (**2**; n = 4) shows a sharp Na^+ selectivity, (**2**; n = 6) shows a broad affinity not only for K^+ but also Rb^+ and Cs^+.[9—11] This suggests that the association between (**2**; n = 6) and alkali metal cations occurs in an 'induced-fit' manner. The trend is readily understandable in terms of the facile molecular motion of each benzene unit which can be detected by dynamic ^1H n.m.r. studies.[13] In fact, (**2**; n = 6) reduces the positive charge at the diazo group but still provides enough room for the transition from the linear Ar–$N^+\equiv N$ to the π-intermediate **A**. The difference between 18-crown-6 and (**2**; n = 6) suggests that mechanism (ii) is responsible for the inhibition by 18-crown-6. The observation that a noncyclic polyether, 1,17-dichloro-3,6,9,12,15-

pentaoxaheptadecane, complexes (**3**) (Table 1) but cannot stabilise (**4**) $\{k/k_0 = 0.98$ at [1,17-dichloro-3,6,9,12,15-pentaoxaheptadecane]/[(**4**)] = 10$\}$ is also in line with this conclusion. This study indicates that mechanism (ii) plays a decisive role in the stabilisation of arenediazonium salts by crown ethers.

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