Cyclodextrin-promoted Free-Radical Dediazoniation of Benzenediazonium Ions

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The effect of β-cyclodextrin (β-CD) on the decomposition of benzenediazonium ions is reported. Dediazoniation of substituted benzenediazonium ions (X = *p*-Me, *p*-Cl, and *p*-NO_2) is accelerated by β-CD and proceeds *via* a radical pathway to form XC_6H_5, irrespective of the nature of the substituent X or the atmosphere (N_2 or O_2). In contrast, trehalose and permethylated β-CD exhibit no enhancement of rate and reduce the yields of XC_6H_5. The cyclodextrin-promoted dediazoniation exhibits both saturation kinetics and competitive inhibition. The observations described are explained in terms of a mechanism involving (i) the specific formation of a *syn*-arylazo ether *via* an inclusion complex formed between the benzenediazonium ion and β-CD and (ii) subsequent homolytic scission of the *syn*-arylazo ether.

In an earlier communication[1] we described how β-cyclodextrin (β-CD) accelerated the rate of replacement of the diazonio group of substituted benzenediazonium ions by hydrogen (hydro-dediazoniation) and suggested that the reaction proceeded *via* a free radical mechanism. It has been shown[2] that the dediazoniation process involves either a heterolytic or homolytic intermediate, and that the mechanism depends on the solvent employed, the substituent on the aromatic ring, the atmosphere, and the pH. For example, reaction in acidic methanol[3–7] gives rise to the product of methoxy-dediazoniation (Ar-OMe) if the reaction is carried out under O_2, and involves an aryl cation intermediate; in contrast, under N_2 the product of hydro-dediazoniation (Ar–H) is mainly formed *via* the radical mechanism. The ionic mechanism predominates for the diazonium ions with electron-donating substituents, while for the substrates bearing electron-withdrawing groups the radical mechanism predominates.[4,5,7] In another example,[8–10] reaction in weakly alkaline aqueous solution (pH 9—10) yields mainly so-called diazo tar and a variety of minor products; the reaction is greatly influenced by O_2, which acts as an autocatalyst.

Below pH 4, dediazoniation offers, exclusively, phenols whereas the formation of *syn*- and *anti*-diazotates predominates above pH 11 (X = *p*-Cl). In the intermediate pH range (pH 5—10) we could control the product distribution of dediazoniation by adding cyclodextrins. Cyclodextrins can form host–guest complexes with many molecules and ions, and affected the rate and/or regioselectivity of several reactions.[11] We now report the results of product and kinetic studies for the cyclodextrin-promoted dediazoniation where the cyclodextrin directs the reaction selectively along one of several possible paths.

Results

Product Analyses for Dediazoniation of Benzenediazonium Ions in the presence of β-CD *and Related Compounds.*—The product distribution of dediazoniation of benzenediazonium ions in aqueous solution is both complex and strongly influenced by the reaction conditions,[2,8–10] a wide variety of reaction products being formed *via* heterolytic and homolytic processes. In the present study the decomposition was carried out at 26 °C to 100% completion; the last traces of the diazonium salt were estimated spectroscopically by dye formation upon coupling with 2-hydroxynaphthalene-3,6-disulphonic acid.[12]

Low-boiling products from hydro-dediazoniation (toluene, chlorobenzene, and nitrobenzene) were directly measured by g.l.c. and the results are listed in Table 1. Reduction of aqueous solutions of cyclodextrins gave high yields of products regardless of atmosphere, pH, and substituents. For example, decomposition of the *p*-chlorobenzenediazonium ion in the absence and in the presence of β-CD yielded 6 and 96% of chlorobenzene, respectively. In the presence of trehalose and permethylated β-CD, the yields of chlorobenzene fell to 38 and 50%, respectively. The yield was little affected, however, by the addition of trehalose to the β-CD solution (84%). In the presence of potassium iodide in the β-CD solution the yield fell from 96 to 68% and the by-products *p*-iodochlorobenzene (19%) and *p*-chlorophenol (small amount) were obtained. Similar results were also obtained for the dediazoniation of *p*-methyl- and *p*-nitro-benzenediazonium ions.

High-boiling products were analysed by high-pressure liquid

Table 1. Hydro-dediazoniation products of substituted benzenediazonium fluoroborates[a]

X	Additive	pH	XC_6H_4-H%
p-Me	β-CD	5.4	87(O_2,[d] 98(N_2)
p-Me	β-CD	7.4	96(air), 70(O_2), 88(N_2)
p-Me	β-CD	10.0	91(air)
p-Me	Trehalose[b]	7.4	40(N_2)
p-Me	β-CD + KI	5.4	46(N_2)[d,e]
p-Me		7.4	Trace
p-Cl	β-CD	5.4	99(O_2),[d] 99(N_2)
p-Cl	β-CD	7.4	96(air), 67(O_2), 90(N_2)
p-Cl	β-CD	10.0	87(air)
p-Cl	α-CD	7.4	91(air)
p-Cl	γ-CD	7.4	80(air)
p-Cl	Trehalose[b]	7.4	38(air), 59(N_2)
p-Cl	Glucose[b]	7.4	51(air)
p-Cl	Permethylated β-CD	7.4	50(air)
p-Cl	β-CD + KI[c]	7.4	68(air)[f]
p-Cl	β-CD + Trehalose	7.4	84(air)
p-Cl		7.4	6(air)
p-NO_2	β-CD	5.4	81(air)
p-NO_2	β-CD	7.4	71(air)
p-NO_2	Trehalose	7.4	27(air)
p-NO_2		7.4	Trace(air)

[a] T = 26.0 °C; ionic strength I = 0.4; reactions mixtures contained 0.01 mmol of diazonium salt and 0.1 mmol of cyclodextrin (CD) in 10 ml of buffer solution. [b] Trehalose and glucose, 0.26 mmol/10 ml buffer solution. [c] KI, 0.3 mmol/10 ml buffer solution of β-CD. [d] From ref. 1. [e] *p*-Iodotoluene and *p*-cresol were also formed in 15 and 25%, respectively. [f] *p*-Iodochlorobenzene was also obtained in 19% yield.

chromatography (h.p.l.c.). The h.p.l.c. analyses of minor products obtained by the reaction of the *p*-chlorobenzenediazonium ion and β-CD showed the formation of 4,4′-dichlorobiphenyl (2.3%) and 4,4′-dichloroazobenzene (trace). In the trehalose solution, dichlorobiphenyl (2.9%) and dichloroazobenzene (0.2%) were obtained. The material balance in the reaction involving β-CD was near quantitative (96%) whilst that involving trehalose summed to less than 40%. Decomposition of the *p*-methylbenzenediazonium ion also gave a product composition similar to that obtained in reaction of the *p*-chlorobenzenediazonium ion. However, the decomposition of the *p*-nitrobenzenediazonium ion in the presence of β-CD and trehalose yielded, besides nitrobenzene, a variety of by-products such as 2.6 and 2.5% of *p*-nitrophenol, 0.9 and 1.2% of 4,4′-dinitrobiphenyl, and 0.1 and 1.0% of 4,4′-dinitroazobenzene respectively, together with some unidentified minor products. The product yield from the reaction of *p*-nitrobenzenediazonium ion and β-CD summed to less than 74%. It appears likely that the *p*-nitrobenzenediazonium ion decomposes by a variety of different reactions, particularly in the presence of O_2 and even in the presence of a ten-fold concentration of β-CD compared with diazonium ion. The material balance deficit, particularly in the absence of β-CD or in the presence of trehalose instead of β-CD, might be due to formation of highly coloured quinonoid products and/or diazo-tars.[8]

Kinetics of Dediazoniation of Benzenediazonium Ions in the Presence of β-CD and Related Compounds.—Figure 1 shows

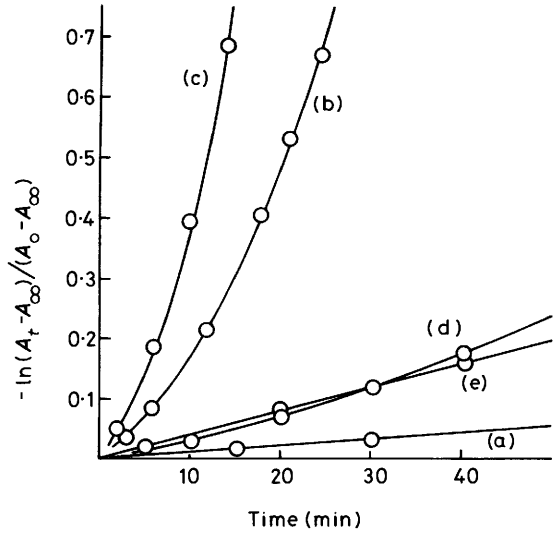


Figure 1. Absorption change (A, at 282 nm) of the *p*-chlorobenzenediazonium ion (6.0×10^{-5}M) with time in air at 26 °C in β-CD solution at pH 7.4. β-CD; (a) 0, (b) 1.2×10^{-3}, (c) 6.0×10^{-3}, (d) 1.2×10^{-3}M and cyclohexanol 1.2×10^{-2}M. (e) Permethylated β-CD 1.2×10^{-3}M was used instead of β-CD.

kinetic results for the dediazoniation of the *p*-chlorobenzenediazonium ion at pH 7.4. The upward curves, indicative of an induction period especially at lower pH,[1,13] are incompatible with simple kinetics and suggest the presence of either a radical chain reaction or autoxidation;[10] this is generally observed in radical dediazoniation. The first-order kinetics held to *ca.* 50% conversion in the presence of β-CD and up to 20—30% conversion in the presence of trehalose. In contrast, the decomposition obeyed first-order kinetics over two half-lives in permethylated β-CD solution or in pure dioxane. By applying the least-squares method, first-order rate constants, k_{obs}, were obtained and are listed in Table 2 when a 20-fold excess of the cyclodextrin (1.2mM) to the diazonium ion was used. β-CD Gave rise to a marked acceleration for the dediazoniation. α- and γ-CDs were also effective in the rate enhancement. For example, *p*-nitro-, *p*-chloro-, and *p*-methylbenzenediazonium ions decomposed 22, 7, and 2 times more rapidly by adding β-CD (1.2mM), respectively. However, no acceleration was observed when trehalose was employed instead of β-CD. Furthermore, decomposition in the presence of permethylated β-CD showed rate retardation, and in pure dioxane the reaction was very slow. Addition of cyclohexanol (a good guest molecule) to a β-CD solution of the diazonium ion, reduced the rate by three-fifths, suggesting that competitive inhibition of dediazoniation was taking place. In contrast, the rate of acceleration by β-CD was little affected by the addition of trehalose. The rate of dediazoniation was found to be accelerated by increasing the amount of β-CD present and finally saturation kinetics were observed as shown in Figure 2;

Table 2. First-order rate constants for dediazoniation of the *p*-chlorobenzenediazonium ion[a]

X	Additive	pH	$k_{obs} \times 10^4$ (s^{-1})	$t_{1/2}$ (min)
p-Me	β-CD	7.4	0.93	67
p-Cl		7.4	0.62	74
p-Cl	β-CD	5.4	0.48	
p-Cl	β-CD	7.4	4.16	25
p-Cl	β-CD	8.8	6.55	19
p-Cl	β-CD	7.4	4.89[b]	32
p-Cl	β-CD + Cyclohexanol	7.4	1.71	51
p-Cl	β-CD + Trehalose	7.4	5.97	20
p-Cl	Trehalose	7.4	0.68	86
p-Cl	Permethylated β-CD	7.4	0.81	147
p-Cl	α-CD	7.4	1.10	45
p-Cl	γ-CD	7.4	1.34	45
p-NO_2	β-CD	7.4	17.5	10

[a] T = 26.0 °C; ionic strength I = 0.4; in air; initial diazonium ion concentration, $=6.00 \times 10^{-5}$M; cyclodextrin (CD) and its derivative, 1.20×10^{-3}M; trehalose, 3.15×10^{-3}M; cyclohexanol, 1.20×10^{-3}M. [b] Under N_2.

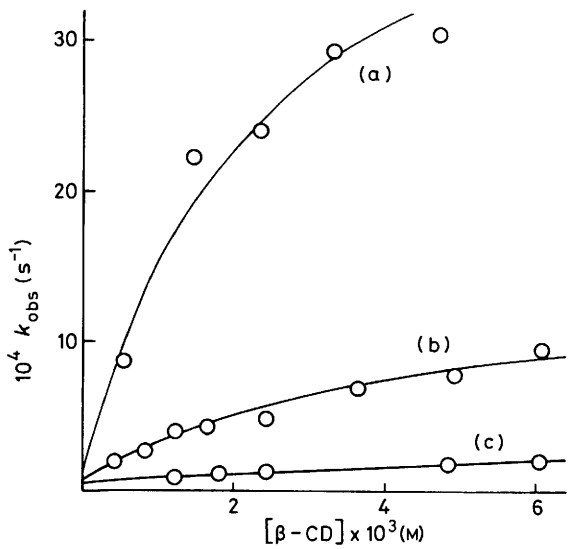


Figure 2. Rate of dediazoniation of *p*-substituted (X) benzenediazonium ions as a function of increasing β-CD concentration at 26 °C, pH 7.4, Sörensen buffer, I = 0.4. (a) X = *p*-NO_2, (b) X = *p*-Cl, (c) *p*-Me

Table 3. Acceleration of dediazoniation of substituted benzenediazonium ions by β-CD[a]

X	$k_2 \times 10^4$ (s^{-1})	$K_d \times 10^3$ (M)	k_2/k_{un}
p-Me	3.39	6.39	7.4
p-Cl	10.2	2.40	16.4
p-Cl[b]	14.1	1.95	7.6
p-NO_2	57.2	2.86	71.5

[a] T = 26.0 °C; ionic strength I = 0.4; pH = 7.4; in air. [b] pH = 8.85.

such kinetics are usually observed in enzyme reactions. Application of the Michaelis-Menten equation, using Lineweaver-Burk plots,[14] to the present reactions, allows us to evaluate their acceleration effects on the basis of the values of the dissociation constant, K_d, and the rate constant for the reaction of the β-CD–diazonium ion complex, k_2, ($k_{obs} - k_{un}$ at the saturation concentration). Their values were obtained from a slope $K_d/k_2 - k_{un}$ and an intercept $1/k_2 - k_{un}$ of a straight line and are shown in Table 3. An examination of Table 3 indicates that strong substituent effects exist for the dediazoniation rate. Since a ρ value obtained by a Hammett plot of log k_2 against σ values is positive (ρ = 1.30), the process is one where the rate-determining step is likely to be favoured by electron-withdrawing substituents. Dissociation constants listed in Table 3 exhibit the effective binding ability of β-CD to the diazonium ions. However, obvious specificity was not observed concerning size or polarity of the substituent.

Discussion

Dediazoniation of benzenediazonium ions in the presence of β-CD gives, exclusively, reduction products (Table 1). This remarkable selectivity was not, however, achieved in the presence of glucose or trehalose (monomeric and dimeric units respectively of cyclodextrin). This result suggests that the ring structure of β-CD plays an important role in the hydrodediazoniation. Competition by the diazonium ion with other substrates for the inclusion complex is largely affected by the size of the substrates. Addition of potassium iodide, which can form an inclusion complex with β-CD,[15,16] to the reaction of the *p*-chlorobenzenediazonium ion reduces the yield of chlorobenzene, whereas the yield is unchanged in the presence of trehalose, the latter being too large to intrude into the cavity of β-CD. These results strongly suggest that β-CD forms an inclusion complex with the diazonium ion. According to the kinetic experiments, β-CD causes a marked acceleration of dediazoniation, whilst trehalose shows no such effect (Table 2). Reactions in the presence of β-CD also shows saturation kinetics (Figure 2) and competitive inhibition in the presence of cyclohexanol (Figure 1 and Table 2). These kinetic results are consistent with the conclusion obtained by product analyses. Accordingly, it seems reasonable to conclude that the high reaction selectivity for hydro-dediazoniation is ascribed to the rapid formation of the inclusion complex between the diazonium ion and β-CD.

In pure dioxane, the *p*-chlorobenzenediazonium ion decomposes slowly in a manner similar to that operating in the aqueous reaction solution containing permethylated β-CD, a compound capable of forming an inclusion complex with benzenes.[17] However, the decomposition is strikingly accelerated by the addition of water,[13,*] in marked contrast with the aqueous reaction in the presence of permethylated β-CD. These observations suggest that the rate enhancement is not detectable in nonpolar solvents such as dioxane and in the presence of permethylated β-CD, *i.e.* the rate acceleration is not attributable to the microsolvent effect of the cyclodextrin as often observed in decarboxylation of phenylcyanoacetic acid anions[18] and benzoylacetic acid anions.[19] Since methylation of the hydroxy groups retards the decomposition and reduces the yield of the reduction product, clearly the hydroxy group of β-CD, as well as the ring structure, is indispensable for the reaction selectivity. Thus, it is claimed that the rate acceleration is brought about by formation of the inclusion complex and the resulting interaction of the diazonium ion with a hydroxy group of β-CD to form an arylazo ether. These steps are analogous to those observed in the stereospecific phenyl ester cleavage.[20]

It has been shown that the dediazoniation in alcoholic solution under N_2 gives the reduction product *via* a radical chain mechanism.[4,6,7,21] The propagation steps proposed are as follows:

$$Ar^{\bullet} + CH_3OH \longrightarrow Ar\text{-}H + {}^{\bullet}CH_2OH \quad (1)$$

$${}^{\bullet}CH_2OH + Ar\text{-}N{=}N^{+} \longrightarrow Ar\text{-}N{=}N^{\bullet} + {}^{+}CH_2OH \quad (2)$$

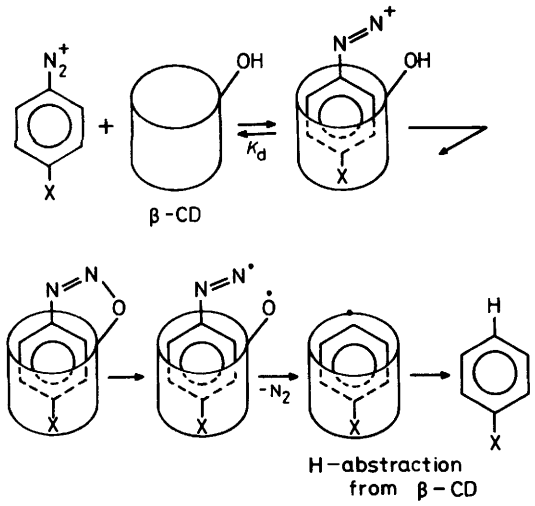
$$Ar\text{-}N{=}N^{\bullet} \longrightarrow Ar^{\bullet} + N_2 \quad (3)$$

It has previously been confirmed by using deuteriated alcohol that the phenyl radical is involved in the dediazoniation.[22] Thus, we also found that the reaction of the *p*-chlorobenzenediazonium ion in the deuterium oxide solution of β-CD yielded nondeuteriated chlorobenzene exclusively (99.4%). This result clearly shows that the *p*-chlorophenyl radical generated abstracts a hydrogen atom from the C–H bond of β-CD, not from the hydroxy group or water. Thus, involvement of radical propagation steps such as (1)—(3) is likely. This is compatible with the kinetic experiment showing the presence of an induction period.

The nature of initiation is, however, less clear. With regard to the mechanism of initiation of the radical dediazoniation in dimethyl sulphoxide (DMSO),[23] hexamethylphosphoric triamide (HMPA),[24] and aqueous phenoxide,[10] it is well documented that there is nucleophilic interaction of the diazonio group with the oxygen of DMSO, HMPA, or phenoxide. Bunnett and Yijima proposed electron transfer from the alcohol to the diazonium ion.[6] Since one-electron oxidation of an alcohol is, from the point of view of its redox potential, an energetically unfavourable process, we prefer the homolytic scission of the arylazo ether, which occurs generally under the alkaline conditions.[25] As suggested by the positive ρ value and the rate increment in alkaline solution, the more electrophilic diazonium ion and the nucleophilic hydroxy group of β-CD are favoured in the arylazo ether formation; thus, this is implicated as a candidate for the rate-determining step. A CPK molecular model suggests that complex formation of the diazonium ion with β-CD leads to preferential formation of the *syn*-arylazo ether rather than the *anti*-arylazo ether because the diazonio and hydroxy groups are fixed in close proximity. Reaction of the benzenediazonium ion with β-CD in aqueous solution, gives as the major initial product, it is assumed, the unstable *syn*-arylazo ether. This, subsequently, undergoes homolytic scission without conversion into the more stable *anti*-arylazo ether as suggested by Broxton and co-workers,[26,27] to form an arylazo radical which enters propagation cycles at step (3). A postulated mechanism for hydrodediazoniation is shown in the Scheme.

It is well established that hydro-dediazoniation in acidic methanol solution is suppressed by O_2 *via* scavenging radicals,[4,6,7] whereas in aqueous solution O_2 gives rise to considerable autoxidation.[10] However, the product selectivity

* In the mixed solution of dioxane and water (20:80) k_{obs} for decomposition of the *p*-chlorobenzenediazonium ion was 2.74×10^{-3} s^{-1} ($t_{1/2}$ = 4.8 min) at 26 °C.



Scheme. The postulated scheme for the β-CD-promoted dediazoniation.

and the rate of the cyclodextrin-promoted dediazoniation are largely unaffected by the atmosphere, presumably because of the protecting effect of β-CD, the formation of the inclusion complex guarding the reactive sites from O_2 attack.[28,29] The protective effect of cyclodextrin is even observed in the reaction using permethylated β-CD in water, where there was retardation of diazonium ion decomposition by the water.

Thus, we conclude that the cyclodextrin-promoted dediazoniation proceeds *via* a sequence of reactions which involve: (i) binding of the diazonium ion with β-CD, (ii) formation of the *syn*-arylazo ether, (iii) generation of radical species by the homolytic cleavage, and (iv) hydrogen abstraction by the phenyl radical so formed. Thus, this hydro-dediazoniation is a novel example of reaction selectivity, *i.e.* the cyclodextrin directs the reaction along one of many possible paths.

Experimental

All the compounds and solvents were reagent grade and were used without purification. Water was purified by deionization and subsequent distillation in an all-glass apparatus. Permethylated β-CD (heneicosakis-2,3,6-*O*-methylcycloheptaamylose) was prepared by the method of Casu *et al.*,[30] Benzenediazonium tetrafluoroborates (X = *p*-Me, *p*-Cl, and *p*-NO_2) were prepared by the literature method[31] and stored at −20 °C on silica gel.

Product Analyses.—β-CD (1.00×10^{-2} M) was dissolved in the buffer solution (pH = 5.40, 7.40, and 8.85: Sörensen buffer, pH = 10.0: Menzel buffer, ionic strength I = 0.4) and kept as a stock solution. The diazonium fluoroborate (0.01 mmol) was transferred to a glass ampoule (20 ml volume) kept in iced water. A β-CD solution (10 ml, 0.1 mmol) was then pipetted in. A stream of O_2 or of deoxygenated N_2 (obtained by passage of 99.999% pure N_2 gas through pyrogallol–KOH solution) was then gently bubbled through the mixture. The ampoule was then sealed and placed in a thermostat bath.

For the quantitative measurement of reduction products (toluene, chlorobenzene, and nitrobenzene; presence confirmed by g.c.–mass spectroscopy), g.l.c. analyses were conducted by means of a Shimazu GC-6A chromatography equipped with the flame ionization detectors and a Shimazu C-RIA integrator, using cyclohexanol as an internal standard (Table 1). The glass column (3.0 mm i.d. × 300 cm) was packed with 10% SE-30 on Chromosorb W. High-boiling products were analysed by means of a Hitachi 633A type h.p.l.c. apparatus equipped with a monitor of variable wavelength and a Shimazu C-RIA integrator. The products were extracted from the reaction mixture with diethyl ether. The chromatogram was obtained through the reversed-phase column, Cosmosil 5C18, eluted with a mixture of MeCN and water.

Reaction Kinetics.—The dediazoniation of benzenediazonium ions was followed spectrophotometrically by monitoring the decrease in absorption. The wavelengths employed with ε in parentheses are as follows: *p*-methylbenzenediazonium ion $\lambda_{max.}(H_2O)$ 280 nm (13 400); *p*-chlorobenzenediazonium ion, 282 nm (13 500); *p*-nitrobenzenediazonium ion, 262 nm (16 300). Plots of $-\ln[A_t) - (A_\infty)]/[(A_0) - A_\infty)]$ *vs.* time were almost linear only in the initial reaction time. In the case of *p*-nitrobenzenediazonium ion, the change of the absorbance was corrected for overlapping nitrobenzene ($\lambda_{max.}$ 270 nm, $\varepsilon_{max.}$ 7 660; ε_{262} 6 830), based on the additivity of each absorbance. The rate constant, k_{obs}, was obtained from the initial portion whose relative coefficient was more than 0.98. The concentration of β-CD and related compounds ($3—60 \times 10^{-4}$ M) were at least five-fold greater than the diazonium salt concentration (6.00×10^{-5} M) in order to maintain pseudo-first-order conditions. The temperature was maintained at 26 ± 0.01 °C by use of a Neslab IC controlled-temperature bath with an external circulating pump. All rates were determined by using a 1-cm standard u.v. quartz cell or a 1-cm anaerobic u.v. quartz cell, which was separated into two compartments (Thunberg tube). Reactions under anaerobic conditions were initiated by mixing the aqueous diazonium salt solutions in the cuvette with the aqueous β-CD solutions in the cell compartment under a N_2 atmosphere.

Reaction in D_2O *Solution.*—The procedure involved the mixing of *p*-chlorobenzenediazonium fluoroborate (0.03 mmol) with β-CD (0.15 mmol) dissolved in D_2O (10 ml) (CEA, 99.85%) as described in product analyses. After decomposition, products were extracted with diethyl ether. The ether extract was concentrated to the volume of *ca.* 1 ml through a Vigreux column, and chlorobenzene was detected by g.c.-mass spectroscopy. The mass spectrometer was operated at an ionizing voltage of 70 eV and the column was packed with 10% SE-30 on Chromosorb W. The content of [^{2}H]chlorobenzene was found to be only 0.58%.

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