

Exclusive Free Radical Dediazonation of Benzenediazonium Ions by β -Cyclodextrin

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Dediazoniation of substituted benzenediazonium ions is accelerated by β -cyclodextrin and proceeds through a radical pathway, forming X-C₆H₄-H whatever the substituent (X) or the atmosphere (N₂ or O₂).

Cyclodextrins form host-guest complexes with many molecules and ions and exert an influence on the rate and/or regioselectivity of several reactions.¹ We now report an example where β -cyclodextrin (β -CD) causes a reaction to proceed along one of two competing pathways. It is well known that dediazonation of benzenediazonium ions in alcoholic solution yields a mixture of the alkyl aryl ether and the reduction product and that the ratio of these products depends on the substituent on the aromatic ring and the atmosphere (N₂ or O₂).² The two distinct mechanisms competing in the reaction are an ionic process forming ethers (or phenols in aqueous solution) and a radical process forming reduction products.

Dediazoniation of substituted benzenediazonium tetrafluoroborates (pH 5.4 buffer, 2.64 mmol/l) was carried out in the presence of β -CD (5 mol. equiv.) at 26 °C. The yield of products was determined by g.l.c. (flame-ionisation detector, SE 30 column), and a selection of the results is shown in Table 1. Although the dediazonation of the *p*-nitrobenzenediazonium ion in the absence of β -CD gave *ca.* 10% of *p*-nitrophenol with many unidentified by-products, the addition of β -CD markedly changed the reaction course to yield *p*-nitrobenzene in 89 and 94% yields under N₂ and O₂, respectively. Similarly, dediazonation of *p*-chloro- and *p*-methylbenzenediazonium ions in the presence of β -CD gave the

Table 1. Dediazoniation products of substituted benzenediazonium fluoroborates in the presence of β -CD.^a

X	Atmosphere	X-C ₆ H ₄ -H	X-C ₆ H ₄ -OH	Others
<i>p</i> -NO ₂	N ₂ ^b	0	8.3	^e
	O ₂	88.9	0	0
<i>p</i> -Cl	N ₂	94.1	0	0
	O ₂	99.1	0	0
<i>p</i> -Me	N ₂	98.6	0	0
	O ₂	80.5	6.1	0
	N ₂ ^c	98.0	0	0
	O ₂	86.7	5.4	0
	N ₂ ^d	46.0	24.7	14.7 ^f

^a Reaction mixtures contained 0.66 mmol of diazonium salt and 3.30 mmol of β -CD in 250 ml aqueous solution, pH 5.4, at 26 °C unless otherwise indicated. ^b In the absence of β -CD. ^c Diazonium salt, 0.33 mmol. ^d KI also present; diazonium salt, 0.33 mmol; β -CD, 1.66 mmol; KI 5.29 mmol. ^e Many unidentified products. ^f *p*-Iodotoluene.

reduction products in excellent yields. The extent of formation of a β -CD-aromatic adduct in the recovered β -CD mixture was less than 1% as determined by u.v. spectroscopy. This forms a striking contrast with the dediazonation in acidic alcohols which yields a mixture of anisoles and reductive products.²

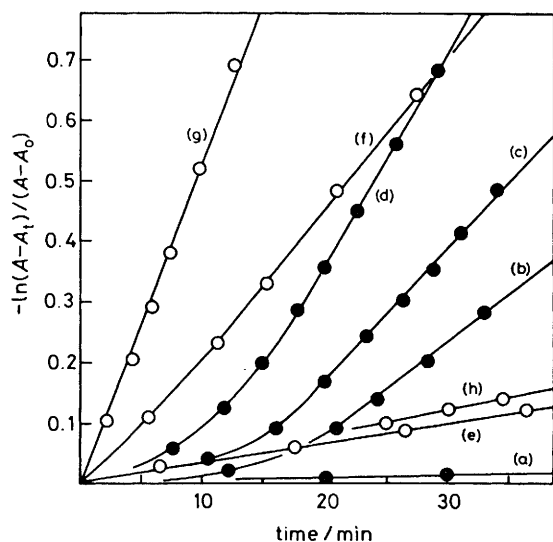


Figure 1. Absorbance change (A , at 260 nm) with time in the dediazonation of the p -nitrobenzenediazonium ion (4.7×10^{-5} mol/l) under air at 26°C in β -CD solution at pH 5.4 (\bullet) and 7.4 (\circ). β -CD at pH 5.4: (a) 0, (b) 4.7×10^{-4} , (c) 9.4×10^{-4} , (d) 2.4×10^{-3} mol/l. β -CD at pH 7.4: (e) 0, (f) 4.7×10^{-4} , (g) 1.4×10^{-3} , (h) 4.7×10^{-4} mol/l and cyclohexanol 4.7×10^{-3} mol/l.

For kinetic analysis, the dediazonation of the p -nitrobenzenediazonium ion was followed by measuring the absorbance change at 260 nm and pH 5.4 and 7.4 under air (Figure 1). The rate of dediazonation was found to be accelerated by increasing concentrations of β -CD and to be saturated at about a fifty-fold excess of β -CD. 'Saturation' kinetics were

observed. For example at pH 7.4 and 26°C the dissociation constant K_d had the value 1×10^{-3} M and the rate constant for decomposition of the complex was 1.5×10^{-3} s $^{-1}$. Cyclohexanol, a good guest of β -CD, effectively suppressed the reaction. This result strongly suggests the formation of an inclusion complex between β -CD and the diazonium ion in this reaction. We also observed a long induction period at pH 5.4 but not at higher pH. Werner and R uchardt obtained a similar result in ethers under N_2 and proposed a radical chain mechanism.³ The dediazonation in acidic methanol² and acidic dioxolan³ was sharply dependent on O_2 , while our results were independent of the atmosphere employed. This suggests that radical species formed are surrounded by cyclodextrin and protected from O_2 , and so the dediazonation in the presence of β -CD may proceed *via* a radical pathway, which would account for the formation of the reduction product. The co-presence of potassium iodide, also a good guest of β -CD, interfered with the formation of toluene from the p -methylbenzenediazonium ion by competition for β -CD and considerable amounts of p -iodotoluene and p -cresol were produced, probably *via* an ionic process. These data show that complex formation with β -CD greatly affects the course of the dediazonation of diazonium ions and causes a radical mechanism in aqueous solution to predominate, whereas an ionic process is normally especially favoured.

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