

ISOTOPE EFFECTS IN AROMATIZATION OF 1,4-DIHYDROBENZENE AND
1,4-DIHYDRONAPHTHALENE WITH QUINONES

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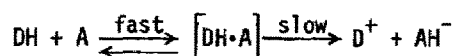
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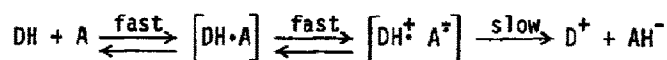
Summary. Aromatization of 1,4-dihydronaphthalene with 2,3-dichloro-5,6-*p*-benzoquinone or chloranil is accompanied with kinetic isotope effects of 9.9 and 8.0 respectively.

The oxidation of 1,4-dihydrobenzene (1) and 1,4-dihydronaphthalene (2) with quinones is of interest in connection with that of dihydropyridines which represent models for biological oxidations involving the pyridine nucleotide coenzymes.¹ Although the latter are generally considered as one-step hydride transfer processes, their mechanism is still not fully understood, and the experimental results are interpretable in different ways. Since the ability of quinones to form charge-transfer complexes is well established² and since formation of radical cations by electron transfer within such complexes of electron-rich aromatics is known to occur,³ the overall hydride transfer can be considered as the result of direct hydride-⁴ (Scheme 1) or sequential electron and hydrogen transfer processes (Scheme 2). Furthermore, although CT-complexes

Scheme 1



Scheme 2

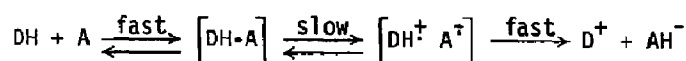


between quinones and dihydroaromatics are formed, their significance for the oxidation remains questionable. A variation of Schemes 1 or 2, consisting in simultaneous transfer of two

hydrogens from the same side of the molecule in the slow step has been proposed for aromatization of 1,4-dihydrobenzene (1) and 1,4-dihydronaphthalene (2).^{5,6} A common feature of the above schemes is that they predict kinetic isotope effects upon replacement of the hydrogens in the methylene groups of 1 or 2 by deuterium or tritium.

The dehydrogenation of 1,4-dihydronaphthalene (2) by chloranil has been investigated by Hashish and Hoodless⁷ in some detail. Surprisingly, these authors found no isotope effect for aromatization of partially tritiated 2 and, consequently, proposed a mechanism where the rate-determining step is associated with slow electron transfer in the CT-complex (Scheme 3):

Scheme 3



An analogy of this mechanism is found in the oxidation of certain trialkyl metal hydrides with tetracyanoethylene and probably also with quinones.⁸ Scheme 3 is however incompatible with the substantial primary isotope effects measured for oxidation of cycloheptatriene,⁹ triphenylcyclopropene,⁹ acenaphthene¹⁰ and 1,4-cyclohexadiene⁶ with DDQ. We considered the possibility of a mechanistic change for aromatization of 1,4-dihydronaphthalene (2) with DDQ and/or chloranil, and therefore reinvestigated the isotope effects on perdeuterated 2¹¹ with both oxidants. The reaction rates for DDQ were measured spectrophotometrically under *pseudo*-first order conditions (excess substrate) at 25°, in benzene⁶ and 1,2-dichloroethane, those for chloranil under second-order conditions (dichloroethane, 120°) by analyzing sealed ampoules by vpc at appropriate time intervals.¹² Table 1 summarizes the experimental results together with data from an earlier communication.⁶ For both oxidants, DDQ and chloranil, we find isotope effects of 9.9 and 8.0, this without correction for contamination of the substrates with unlabelled material (1-2%).

The discrepancy of our results compared with those of Hashish and Hoodless⁷ can be explained on the grounds of differences in the experimental set-up. While our work is based on molecules with more than 98% D-incorporation, they used T-labelling, where only a fraction of the substrate molecules were labelled. The latter procedure is adequate if the molecules under

Table 1. Rate constants and isotope effects for aromatization of 1,4-dihydrobenzene (1) and 1,4-dihydronaphthalene (2)

Substrate	Oxidant	Conditions	$10^2 k [M^{-1} s^{-1}]$	k_H/k_D	Comment
1,4-Dihydrobenzene (<u>1</u>)	DDQ	Benzene, 25°	2.85	-	Ref. 8
1,4-Dihydrobenzene-d ₆	"	" "	1.67	1.70	" "
1,4-Dihydrobenzene-d ₈	"	" "	0.31	9.2	" "
1,4-Dihydro-naphthalene (<u>2</u>)	"	Dichloroethane, 25°	124.5	-	
1,4-Dihydro-naphthalene-d ₁₀	"	" "	12.57	9.9	
1,4-Dihydro-naphthalene (<u>2</u>)	Chloranil	" 120°	1.235	-	
1,4-Dihydro-naphthalene-d ₁₀	"	" "	0.255	4.84	$k_H/k_D = 8.0$ at 25°

investigation have only one reactive site. In the case of 1 and 2 however, there are four hydrogens available. If we assume a simple hydride transfer mechanism, the maximum primary isotope effect will not exceed 1.33 because, irrespective of the rate of breaking of the CD bond, there are still three hydrogens available which are essentially unaffected by D or T-substitution. Therefore, the increase in specific activity of T-labelled 2 will be very small, particularly at low conversion, and for this reason it must have escaped detection.¹³ These considerations are corroborated by the observation of the small kinetic isotope effect of only 1.70 for reaction of 1-d₆ containing one hydrogen in each methylene group with DDQ (Table 1). A similar argument can be developed for the mechanism consisting in simultaneous transfer of two *cis*-hydrogens.

From our results it follows that aromatization of 1 and 2 with DDQ or chloranil does not proceed *via* electron transfer in the rate-determining step. The mechanism according to Scheme 3 appears to be not general for hydrogen transfer to quinones. It is clear, however, that the isotope effects of 1 and 2 cannot differentiate between Schemes 1 and 2, nor provide further insight into the nature of the CH-bond breaking step.

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- 11) 1,4-Dihydronaphthalene-d₁₀ was readily prepared by reduction of naphthalene-d₈ with Na in EtO₂d, cf. E.S. Cook & A.J. Hill, *J. Am. Chem. Soc.* **62**, 1995 (1940). Pure 1,4-dihydronaphthalene-d₁₀ was obtained by preparative vpc.
- 12) Initial concentrations varied between $9.6 \cdot 10^{-3}$ and $1.1 \cdot 10^{-2}$ M for 2 and $4.9 \cdot 10^{-3}$ and $1.9 \cdot 10^{-2}$ M for chloranil. The second-order rate constants given represent an average value from three runs with standard deviation of the mean of 0.033.
- 13) For the hydride mechanism, assuming the CT bond totally unreactive, the specific activity of 2, after 42% conversion, will increase by a factor of 1.2 at most.

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