Tetrahedron Vol. 35, pp. 1737 to 1743

0040-4020/0715-1737/$02.00/0

TRANSFER HYDROGENATION AND TRANSFER HYDROGENOLYSIS—21

DEHYDROGENATION OF ALCOHOLS BY QUINONES

AKIRA OHKI, TAKESHI NISHIGUCHI* and KAZUO FUKUZUMI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

(*Received in Japan* 22 *November* 1978)

Abstract—Dehydrogenation of benzyl-type alcohols and hydroaromatic compounds by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and tetrachloro-*p*-benzoquinone were examined, and the hydrogen transfer from 1-phenyl-1-propanol to DDQ was investigated in detail. The yield of the propiophenone increased when solvents which would be expected to increase the concentration of the charge transfer complex between the alcohol and DDQ were used. Initial rates of the reaction in dioxane were proportional to the concentration of the hydrogen donor and that of the hydrogen acceptor. In the dehydrogenation of several *para*- or *meta*-substituted 1-phenyl-1-propanols at 60°, −3.30 was obtained as a value of reaction constant. Relative rates of the reaction of PhCH(OH)Et, PhCH(OD)Et, PhCD(OH)Et, and PhCD(OD)Et were 8.9, 9.1, 1.0 and 1, respectively. This result suggests that the transfer of the H atom attached to the α-carbon of the alcohol is the rate-determining step. This and some other results support a two-step ionic mechanism for the dehydrogenation of alcohols.

The thermal hydrogen transfer from dihydrobenzenes and steroids to high potential quinones has been studied.[1] However, the reports of the hydrogen transfer from alcohols to quinones are relatively scarce[2] and the mechanisms of this reaction seems to have been investigated but little.[1,2a]

In a previous paper, we reported the hydrogen transfer from benzyl-type alcohols to tetracyanoethylene (TCNE)[3] and this study was undertaken to compare the dehydrogenation of alcohols by quinones with that by TCNE.

RESULTS AND DISCUSSION

Hydrogen-donating ability. As representatives of quinones, 2,3 - dichloro - 5,6 - dicyano - *p* - benzoquinone (DDQ) and tetrachloro-*p*-benzoquinone (chloranil) were chosen, and dehydrogenations by them were investigated. At first, the susceptibility of organic compounds to the dehydrogenation by DDQ was examined under the following conditions: a hydrogen donor (0.05 M) and DDQ (0.05 M) were heated at 60° for 2 hr in dioxane. This was used as a solvent for dehydrogenation by DDQ.[1b] In these dehydrogenations, DDQ was reduced to 2,3-dichloro-5,6-dicyanohydroquinone which was isolated as a white crystalline compound and identified by m.p. and IR spectrum. Quinones, including DDQ, have been reported to undergo side reactions such as Diels–Alder, addition, and substitution reactions.[1] In some cases extensive side reactions occur. We have determined not only the yield of dehydrogenation product but also the amount of starting material that remains. Several hydroaromatic compounds and alcohols were examined as hydrogen donors. They all gave the dehydrogenated products, aromatic or carbonyl compounds, respectively.

As shown in Table 1, the yield of dehydrogenation products decreased in the following order: 9,10-dihydroanthracene > 1,4-dihydronaphthalene > indoline > cinnamyl alcohol > 1,2,3,4-tetrahydroquinoline > 1,2-dihydronaphthalene > 2,5-dihydrofuran > 1-phenyl-1-propanol. Side reactions were extensive in the reaction of indoline and cinnamyl alcohol.

When a hydrogen donor (0.2 M) and chloranil (0.2 M) were heated at 140° for 3 hr in dioxane, tetrachlorohydroquinone was isolated along with the dehydrogenation products anticipated. As shown in Table 1, the hydrogen-donating ability of organic compounds decreased in the following order: 9,10-dihydroanthracene > indoline > cinnamyl alcohol > 1,4-dihydronaphthalene > 1,2,3,4-tetrahydroquinoline > 1,2,3,4-tetrahydrocarbazole > 2,5 - dihydrofuran > 1,2 - dihydronaphthalene > 1,2 - dihydro - 1,1 - dimethylnaphenalene > 1 - phenyl - 1 - propanol. Side reactions were considerable in the reaction of tetrahydrocarbazole, 1,4 - and 1,2 - dihydronaphthalene and 1,2 - dihydro - 1,1 - dimethylnaphthalene. In the reaction of the dimethyl compound rearrangement of a Me group occured and 1,2-dimethylnaphthalene was formed as in the dehydrogenation by DDQ[4] and TCNE.[3] This fact suggests that an electron deficient species is formed by the hydride abstraction at the 2-position of the hydrogen donor.[4] Taking into account of the steric hindrance of the two Me groups, the reactivity of 1,1-dimethyl derivative is not much less than that of 1,2-dihydronaphthalene. Therefore, it is suggested that these two compounds were dehydrogenated by the same mechanism and that the hydrogen abstraction from the 2-position of the 1,2-dihydronaphthalenes is the rate-determining step.

DDQ was used as a representative of quinones in the experiments described because it has been used most widely in dehydrogenations by quinones. 1-Phenyl-1-propanol was employed as a hydrogen donor because (1) mechanistic studies of thermal hydrogen transfer from alcohols seem to be relatively scarce,[1,2b] (2) the alcohol undergoes few side reactions and (3) ring-substituted 1-phenyl-1-propanols are easy to be obtained.

Reaction solvents. Solvent effects were investigated to discuss the mechanism of the dehydrogenation. Solvents that dissolved DDQ well and did not cause observable side reactions were chosen, and the results are summarized in Table 2.

It has been proposed that the dehydrogenation by quinones occurs via the formation of charge-transfer (CT) complexes.[1] Therefore, the influence of solvents

Table 1. Dehydrogenation by quinones

Hydrogen donor	Hydrogen acceptor	Yield of dehydrogenation product (%)	Recovery of hydrogen donor (%)
9,10-Dihydroanthracene	DDQ[a]	64	27
1,4-Dihydronaphthalene		61	33
Indoline		61	0
Cinnamyl alcohol		54	14
1,2,3,4-Tetrahydro-quinoline		46	50
1,2-Dihydronaphthalene		38	62
2,5-Dihydrofuran		31	70
1-Phenyl-1-propanol		15	79
9,10-Dihydroanthracene	Chloranil[b]	95	6
Indoline		93	7
Cinnamyl alcohol		92	0
1,4-Dihydronaphthalene		79	4
1,2,3,4-Tetrahydro-quinoline		74	27
1,2,3,4-Tetrahydro-carbazole		35	41
2,5-Dihydrofuran		35	63
1,2-Dihydronaphthalene		28	60
1,2-Dihydro-1,1-dimethylnaphthalene[c]		16	71
1-Phenyl-1-propanol		9	87

[a] DDQ (0.05 M) and a hydrogen donor (0.05 M) were heated at 60°C for 2 h in dioxane.

[b] Chloranil (0.2 M) and a hydrogen donor (0.2 M) were heated at 140°C for 3 h in dioxane.

[c] Dehydrogenation product was 1,2-dimethylnaphthalene.

may be interpreted by the stabilization of the CT complex between DDQ and 1-phenyl-1-propanol and/or other active species including the transition state of the rate-determining step of the reaction by solvation. We tried to identify the absorption band attributable to the complex between DDQ and 1-phenyl-1-propanol in some solvents, however the band could not be identified clearly, partly because of the existence of the strong bands owing to the complexes between DDQ and the solvents. Consequently, the relative amount of the complex between DDQ and hexamethylbenzene was measured to estimate roughly the dependence of the ease of the DDQ/1-phenyl-1-propanol complex formation on the solvents. It has been reported that the wavelength of the absorption of the DDQ/hexamethylbenzene complex in dichloromethane is 629 nm.[5] The wavelength at the maximum absorption (λ_{CT}) and the absorbance ($\log(I_0/I)$) are shown in Table 2, along with the transition energy for the CT band of pyridinium N-phenolbetaine (E_T) in a given solvent.[6] The latter parameter is regarded as a quantitative measure of ionizing power of solvents. The yield of propiophenone may be explained by the absorbance, except for the reaction in benzene, and this result supports the assumption that the hydrogen transfer reaction proceeds via the formation of the complex which lies before the rate-determining step of the reaction. The yield of the ketone and the absorbance may also be correlated with E_T in a rough sense. This result suggests that the complex and/or the transition state of the rate-limiting step are solvated and considerably polarized. The low yield of the ketone in benzene may be due to the low value of E_T.

The basicity of solvents seems to be hardly correlated with the yield of the ketone.

Effect of additives. The effect of additives was investigated and the results are summarized in Table 3. In

Table 2. Effect of solvents[a]

Solvent	Yield of ketone (%)	Recovery of alcohol (%)	λ_{CT}[b] (nm)	log (I_0/I)[c]	E_T[d] (kcal mol^{-1})
Chloroform	51	41	625	1.43	39.1
Dichloromethane	33	59	623	1.42	41.1
Chlorobenzene	26	61	619	1.24	37.5
Ethyl acetate	20	77	583	0.29	38.1
Tetrahydrofuran	16	74	589	0.24	37.4
Dioxane	15	79	587	0.18	36.0
Benzene	15	67	608	0.68	34.5
Phenetole	15	80	e	e	

[a] DDQ (0.05 M) and 1-phenyl-1-propanol (0.05 M) were heated at 60°C for 2 h.

[b] Wavelength of the absorption maxima of the band owing to the CT complex between DDQ (1 mM) and hexamethylbenzene (1 mM).

[c] Absorbance of the band described above.

[d] Molar transition energy of pyridinium N-phenolbetaine in the designated solvents.

[e] The band was covered by absorption of the complex between DDQ and the solvent.

the dehydrogenation by quinones the mechanism involving radical process has been proposed.[7] Therefore, the validity of the radical mechanisms was examined in our system. *p*-t-Butylphenol, which is an inhibitor of radical reactions, did not retard the dehydrogenation. However, hydroquinone and pyrocatechol hindered it. The blocking effect of the latter two radical inhibitors may be due to side reactions because they reacted with DDQ to give precipitates even in the absence of 1-phenyl-1-propanol. The addition of α,α'-azobisisobutyronitrile (AIBN) and benzoyl peroxide did not promote markedly the reaction even at 110°. A large negative value for the activation entropy (as seen later) also suggests that a radical process is not likely,[8] although the existence of some radical intermediates is not completely ruled out.

It has been reported that the dehydrogenation of 1,4-dihydronaphthalenes by quinones is catalyzed by acids.[9] However, in our system the addition of acetic and dichloroacetic acid did not raise the yield of the ketone but lowered it. This effect of the acids may be interpreted by side reactions involving the acids and/or by the protonation on 1-phenyl-1-propanol which would reduce the hydrogen-donating power of the alcohol.

2-Butanol promoted the dehydrogenation but propiophenone retarded it.

Measurement of reaction rates. In Fig. 1 a plot of the yield of propiophenone against the reaction time is shown. At the initial stage of the reaction the yield of the ketone was proportional to the time up to about 30% in this case. The initial rate of the reaction was derived from the linear part of the plot.

In the dehydrogenations of dihydrobenzenes by quinones[1] and steroid alcohols by DDQ,[2b] second-order kinetics has been reported. In our system also, the initial rate was found to be proportional to the concentration of DDQ and 1-phenyl-1-propanol up to 0.05 M, as shown in

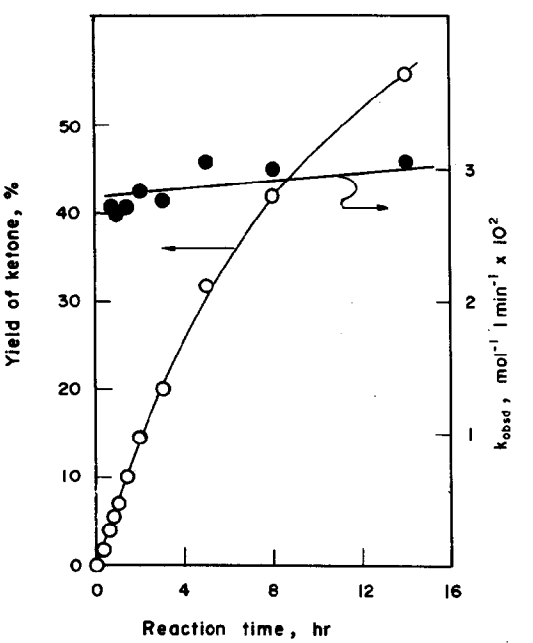


Fig. 1. Plots of the yield of ketone (○) and rate-constant (●) vs reaction time. DDQ (0.05 M) and 1-phenyl-1-propanol (0.05 M) were heated at 60° in dioxane.

Fig. 2. When the concentration of DDQ was 0.05 M and that of the alcohol was higher than 0.07 M, the initial rate deviated upward from the linear line and this phenomenon might be explained by the promoting effect of alcohols shown by the addition of 2-butanol (Table 3). The initial rate did not deviate from the linearity in higher concentration of the reactants than 0.05 M. Therefore,

Table 3. Effect of additives[a]

Additive	Yield of ketone (%)	Recovery of alcohol (%)
None	15	79
2-Butanol	19	77
p-tert-Butylphenol	16	81
N,N-Dimethylacetamide	12	82
Benzoyl peroxide[b]	9	85
Acetic acid	8	84
Dichloroacetic acid	8	70
Propiophenone	2	77
Propiophenone[c]	9	80
Hydroquinone	0	100
Pyrocatechol	0	100
None[d]	9	92
AIBN[d]	12	92
Benzoyl peroxide[d]	8	90

[a] DDQ (0.05 M), 1-phenyl-1-propanol (0.05 M), and an additive (0.1 M) were heated at 60°C for 2 h in dioxane.

[b] The amount of this additive was 0.05 M.

[c] The amount of this additive was 0.025 M.

[d] DDQ (0.025 M), 1-phenyl-1-propanol (0.05 M), and an additive (0.01 M) were heated at 110°C for 9 min.

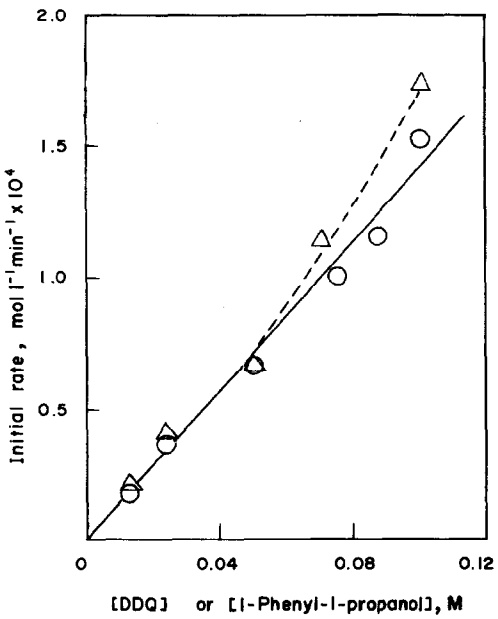


Fig. 2. Plots of initial rate vs the concentration of DDQ (○) and 1-phenyl-1-propanol (△); the concentration of the other reactant was 0.05 M, the temperature was 60°, and the solvent was dioxane.

the concentration of the DDQ/1-phenyl-1-propanol complex would not be so high because the formation of the complex in high concentration would lead to deviation from linearity.

As already mentioned, the rate is inferred to be correlated to the concentration of the CT complex. Therefore, the reaction scheme and the rate may be expressed as follows:

$$\text{DDQ} + \text{A} \overset{K}{\rightleftarrows} \text{complex} \xrightarrow{k} \text{products}$$

$$\text{Rate} = k_{obsd}[\text{DDQ}][\text{A}] = k[\text{complex}] = kK[\text{DDQ}][\text{A}]$$

where A, K, k and k_{obsd} represent 1-phenyl-1-propanol, the equilibrium constant between the reactants and the CT complex, the rate constant of the rate-determining step, and the observed second-order rate constant, respectively.

The value of the observed rate constants were found to be almost unchanged up to 55% conversion as shown in Fig. 1. This result indicates that side reactions and autocatalysis by the reaction products are not important in the initial stage of the reaction.

Initial rates were measured at temperatures ranging from 50 to 90° in dioxane. A plot of the logarithms of k_{obsd} against the reciprocal of the reaction temperatures (°K) showed a good linear relationship indicating that the

kinetics of this system are not complicated. From the plot, 14.6 kcal mol^{-1}, 13.9 kcal mol^{-1} and −35.0 eu were obtained for the Arrhenius energy of activation, the activation enthalpy and the activation entropy at 70°, respectively The values of these kinetic parameters approximately are comparable to those in the hydrogen transfer from 1,4-dihydronaphthalenes to quinones[9] and in the one from 1-phenyl-1-propanol to TCNE.[3] Such a similarity of the values would suggest a resemblance between the reaction mechanisms. The large negative value of activation entropy may show that the transition state of the rate-determining step is highly ordered and does not involve free radical species.[8]

Effect of substituents. In a review, Jackman has reported that in the dehydrogenation of a series of 6- and 7-substituted 1,2-dihydronaphthalenes by a quinone, the rates are correlated with the Hammett σ, or still better with the σ^+ values of the substituents, and a large negative ρ value obtained (−2.7) is indicative of a fairly high sensitivity of the reaction toward the changes in substituents.[1a]

In order to discuss the electronic effect in the dehydrogenation of alcohols by quinones, initial rates of the reaction of DDQ with *m*- or *p*-substituted 1-phenyl-1-propanol were measured. Using least squares, the logarithms of the second-order rate constants were correlated to σ to give ρ value of −3.30, and a correlation coefficient, r of −0.952, while correlating to σ^+ gave $\rho = -2.76$ and $r = -0.952$ (Fig. 3). It is inferred from the fairly large negative ρ values that the transition state of the rate-limiting step has a greater charge separation than the species which lie before the rate determining step. These ρ values are comparable to the value reported by Jackman[1a] and to the ones obtained in the reaction between TCNE and 1-phenyl-1-propanols.[3] The resemblance of the ρ values suggests that the mechanisms of the dehydrogenation of alcohols by quinones and TCNE and that of 1,2-dihydronaphthalenes by quinones are mutually similar.

Kinetic isotope effect. Müller has found that the rate of the dehydrogenation of 1,4-cyclohexadiene by DDQ is ten times higher than that of 1,4-cyclohexadiene-d_8, and based on such an enormously large isotope effect, assumed that the cleavages of C_1–H and C_4–H bonds occur simultaneously at the rate-determining step.[10] Burstain and Ringold have also reported a primary kinetic isotope effect (*ca.* five hold) in the dehydrogenation of 3α-deuterio-Δ^4-3-hydroxy steroids by DDQ.[2b] However, Hashish and Hoodless observed no primary isotope effect in the hydrogen transfer from 1,4-dihydronaphthalene (RH_2) to chloranile (Q) in phenetole, and concluded that the rate-determining step is not at the hydrogen transfer steps (3 and 4) but at the electron-transfer step between the CT complexes (2).[11]

$$RH_2 + Q \overset{1}{\rightleftharpoons} [RH_2 \cdot Q] \overset{2}{\rightleftharpoons} [RH_2^+ \cdot Q^-] \overset{3}{\longrightarrow} RH^+ + QH^- \overset{4}{\longrightarrow} R + QH_2$$

We measured the initial rates of the reaction of PhCH(OH)Et, PhCH(OD)Et, PhCD(OH)Et and PhCD(OD)Et with DDQ at 60° in dioxane and found that the relative rates of them were 8.9, 9.1, 1.0 and 1, respectively. This result shows that a primary isotope effect was observed in the transfer of the hydrogen attached to the α-carbon of the alcohol while no effect was detected in that of the H atom of the OH group. This means that the cleavage of the C_α–H bond is of primary importance in the rate-determining step while that of the O–H bond is only of secondary importance or is not involved in the step.

Analogous result was also obtained in the dehydrogenation by TCNE, although the values of the primary kinetic isotope effect were smaller.[3]

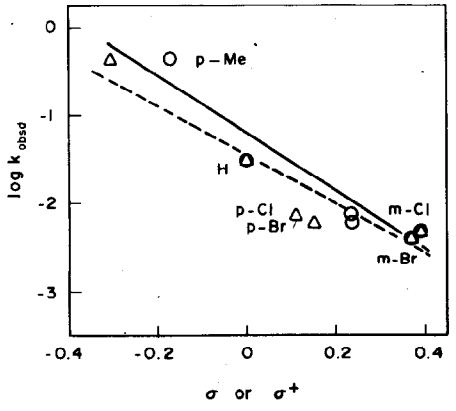


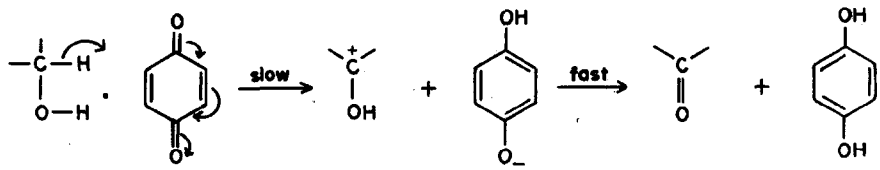
Fig. 3. Plots of k_{obsd} vs σ (—○—) and σ^+ (---△---). DDQ (0.05 M) and a para- or meta-substituted 1-phenyl-1-propanol (0.05 M) were heated at 60° in dioxane.

MECHANISTIC DISCUSSION

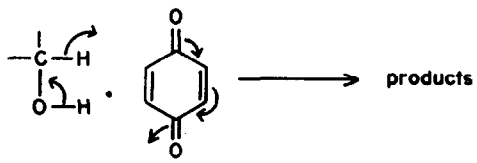
As for the hydrogen transfer from 1,4-cyclohexadienes to *p*-quinones, four reaction mechanisms have been proposed. Braude *et al.* came to the conclusion that the dehydrogenation consists of a rate-limiting hydride anion transfer from the hydrogen donor to the hydrogen acceptors, leading to the formation of a delocalized carbonium ion which loses a proton in a subsequent rapid step (two-step ionic mechanism).[1a] They considered the possibility of forming benzenes in a single-step reaction in which two *cis* H atoms attached to C_1 and C_4 of 1,4-cyclohexadienes are transferred to the O atoms of *p*-quinones (concerted 1,6-reduction). However, they rejected this cyclic mechanism on the basis of the observation that the dehydrogenation rates for 1,2- and 1,4-dihydronaphthalenes by 1,2- and 1,4-quinones are insensitive to the internuclear distance of the H atoms undergoing transfer and to that of the two quinone O atom.[12] Further, they considered a one-step mechanism involving solvents as proton acceptors (concerted solvent mechanism), but they denied it also, when they found that the rate of the dehydrogenation shows little dependency on the basicity of solvents.[13] Stoos and Rocek found that the dehydrogenation by DDQ of 1,4-cyclohexadienes, which can form aromatic hydrocarbons in a one step dehydrogenation, is about three orders of magnitude faster than that of 1,4-dienes, which cannot form aromatics in a single-step reaction.[14] They concluded that the dehydrogenation must involve the synchronous cleavage of the C_1–H and C_4–H bonds of 1,4-cyclohexadienes. They considered the possibility of concerted 1,4-reduction mechanism in which one of the two H atoms of the donors transfers to one of the carbonyl oxygens of *p*-quinones and the other hydrogen to the β-position of α,β-unsaturated carbonyl unit of *p*-quinones in a single-step and the 4 - hydroxy - 2,4 -

cyclohexadien - 1 - ones that form isomerize rapidly to hydroquinones (concerted 1,4-reduction mechanism). They preferred this mechanism to the concerted 1,6-reduction mechanism because the former is symmetry allowed while the latter is symmetry forbidden.[14] Later, Müller supported most strongly the concerted solvent mechanism by comparing the rates of dehydrogenation of various hydrogen donors by DDQ.[10] As for mechanisms of the dehydrogenation of alcohols by quinones, Braude *et al.*, have proposed two-step ionic mechanism on the basis of the analogy of the dehydrogenation of alcohols by tetrachloro-*o*-benzoquinone to that of hydroaromatic compounds by quinones.[2a] Burstain and Ringold have supported it in the reaction of Δ^4-3-hydroxy steroids with DDQ, basing mainly on the kinetic isotope effect described before.[2b]

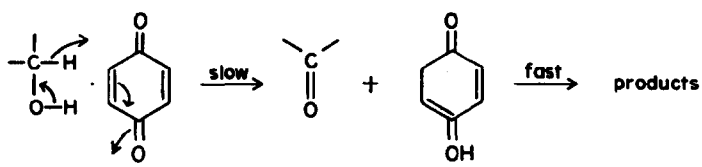
Based on these studies, the following five reaction mechanisms (Schemes 1–5) may be considered for the hydrogen transfer from alcohols to *p*-quinones. Schemes 1–3 and 5 correspond to the two-step ionic mechanism, the concerted 1,6-reduction mechanism, the concerted 1,4-reduction mechanism, and the concerted solvent mechanism in the dehydrogenation of 1,4-dihydrobenzenes by *p*-quinones, respectively. Among these schemes, Scheme 1 is most likely because (1) a highly chargeseparated transition state should be considered from the fairly large negative values of ρ, (2) a primary kinetic isotope effect was observed in the C_α–H bond cleavage of 1-phenyl-1-propanol and was not in the O–H bond cleavage, (3) no phenomenon which conflicts with this scheme was observed. In this scheme, possibility of the solvent participation in the subsequent rapid proton transfer step is not ruled out. In the concerted cyclic mechanisms, Schemes 2 and 4 are symmetry allowed although Scheme 3 is not. However, these scheme are not likely because no primary kinetic isotope effect has been observed in the transfer of the OH hydrogen of 1-phenyl-1-propanol, and that the transition state of the



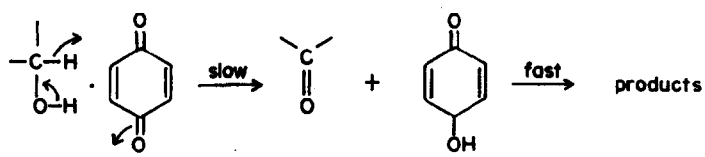
Scheme 1.



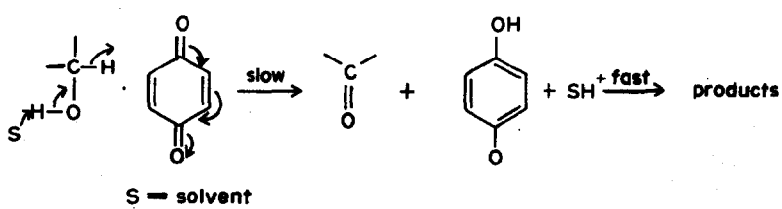
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

rate-determining step is considered to be much more polarized than those for these concerted processes. Scheme 5 is a two-step mechanism in which the rate-limiting step is at a concerted process involving a solvent (S) as a proton acceptor. This scheme is presumed not to be reasonable because of the same reasons as in Schemes 2–4. Furthermore, Scheme 5 would be less consistent with the fact that the basicity of solvents was hardly correlated with the yield of propiophenone.

In conclusion, the mechanism of the dehydrogenation of 1-phenyl-1-propanol by DDQ seems to be similar to that by TCNE.

EXPERIMENTAL

Materials. 1,2-Dihydro-1,1-dimethylnaphthalene,[4] and *p*-methyl,[15] *p*-chloro,[15] *m*-chloro,[15] *p*-bromo[16] and *m*-bromo[17] derivatives of 1-phenyl-1-propanol were prepared by the methods reported in the literature. The preparation and purity of the deuterated 1-phenyl-1-propanols were described in the previous paper.[3] All the reagents purchased were purified by distillation or recrystallization.

An example of dehydrogenation by DDQ. DDQ (11.4 mg, 0.05 mmol) and 1-phenyl-1-propanol (6.9 μl, 0.05 mmol) were put into a Pyrex glass tube which had been sealed at one end. Dioxane was added, and the total volume of the soln was made to 1.0 ml. The tube was sealed under vacuum after a freeze-pump-thaw cycle using a vacuum line and a liquid N_2 bath. The sealed tube was heated in a water bath kept at $60 \pm 0.5°$ for 2 hr. The mixture was submitted to glc analysis, which was performed using 5 μl of phenylcyclohexane as an internal standard and a 1 m × 6 mm stainless column packed with 12% diethylene glycol succinate on Diasolid L.

The other dehydrogenations were carried out in a similar way.

An example of kinetic measurement. Five sealed tubes prepared by the method described above were heated at $60 \pm 0.5°$ for 0.5, 1, 1.5, 2 and 2.5 hr, respectively. Each mixture was submitted to the glc analysis. Initial rate was derived from the gradient of the yield of propiophenone against time plot.

REFERENCES

[1a]L. M. Jackman, *Adv. Org. Chem.* 2, 329 (1960); [b]D. Walker and J. D. Hiebert, *Chem. Rev.* 67, 153 (1967); [c]A. B. Turner, *Synthetic Reagents* Vol. III, Chap. 2. Wiley, New York (1977).

[2a]E. A. Braude, R. P. Linstead and K. R. Wooldrige, *J. Chem. Soc.* 3070 (1956); [b]S. H. Burstein and J. Ringold, *J. Am. Chem. Soc.* 86, 4952 (1964); [c]G. M. Pilling and F. Sondheimer, *Ibid.* 93, 1977 (1971); [d]D. R. Brown and A. B. Turner, *J. Chem. Soc.* Perkin II, 1307 (1975); [e]D. Burn, V. Petrow and G. O. Weston, *Tetrahedron Letters* No. 9, 14 (1960); [f]H. D. Becker and T. Bremholt, *Ibid.* 197 (1973); [g]J. Iwamura and N. Hirano, *Ibid.* 2447 (1973); J. Iwamura, *Nippon Kagaku Kaishi* 1003 (1977); [i]J. Iwamura, *Ibid.* 846 (1978); [j]K. Mori, *Agr. Biol. Chem.* 37, 2899 (1973); [k]H. D. Becker and E. Alder, *Acta Chem. Scand.* 15, 218 (1961).

[3]T. Nishiguchi, A. Ohki, H. Sakakibara and K. Fukuzumi, *J. Org. Chem.* 43, 2803 (1978).

[4a]E. A. Braude, L. M. Jackman, R. P. Linstead and G. Lowe, *J. Chem. Soc.* 3133 (1960); [b]J. R. Barnard and L. M. Jackman, *Ibid.* 3110 (1960).

[5]P. R. Hammond, *J. Chem. Soc.* 3113 (1963).

[6]C. Reichardt, *Angew. Chem.* Int. Ed. Engl. 4, 29 (1965).

[7]H. D. Reid, M. Frazer, A. A. S. Payne and R. G. Sutherland, *Tetrahedron Letters* 530 (1961).

[8]E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.* 3574 (1954).

[9]E. A. Braude, L. M. Jackman and R. P. Linstead, *Ibid.* 3548 (1954).

[10]P. Müller, *Helv. Chim. Acta* 56, 1243 (1973).

[11]Z. M. Hashish and I. M. Hoodless, *Can. J. Chem.* 54, 2261 (1976).

[12]E. A. Braude, L. M. Jackman, R. P. Linstead and J. S. Shannon, *J. Chem. Soc.* 3116 (1960).

[13]E. A. Braude, L. M. Jackman and R. P. Linstead, *Can. J. Chem.* 3564 (1954).

[14]F. Stoos and J. Rocek, *J. Am. Chem. Soc.* 94, 2719 (1972).

[15]C. Bocard, M. Davidson, M. Hellin and F. Cossemant, *Bull. Soc. Chim. Fr.* 163 (1971).

[16]J. Seyden-Penne and C. Schaal, *Bull. Soc. Chim. Fr.* 3653 (1969).

[17]J. Frejka and H. Zámiš, *Cas Cesk. Lek.* 63, 157 (1950); *Chem. Abstr.* 47, 2131e (1953).