Transfer Hydrogenation and Transfer Hydrogenolysis. 16. Dehydrogenation by Tetracyanoethylene

Takeshi Nishiguchi,* Akira Ohki, Hiromitsu Sakakibara, and Kazuo Fukuzumi

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan
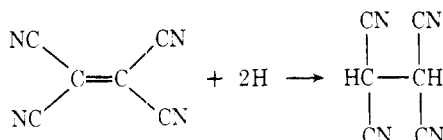
Several benzyl-type alcohols and hydroaromatic compounds were dehydrogenated by tetracyanoethylene (TCNE). The hydrogen transfer from 1-phenylpropanol was studied in detail. The yield of propiophenone increased when solvents which seem to increase the concentration of the complex between TCNE and the alcohol or to stabilize ionic species were used. Initial rates of the reaction were proportional to the concentration of the hydrogen donor and the hydrogen acceptor. In the reaction of several para- or meta-substituted 1-phenylpropanols in dioxane at 100 °C, −3.13 was obtained as a value of the reaction constant. Relative rates of the reaction of PhCH(OH)Et, PhCH(OD)Et, PhCD(OH)Et, and PhCD(OD)Et were 2.8, 2.5, 1.1, and 1, respectively. This means that the transfer of the hydrogen attached to the α position of the alcohol is the rate-determining step. Discussions about the mechanism of this hydrogen-transfer reaction are given.

The thermal hydrogen transfer from some types of organic compounds to high-potential quinones is well known.[1] However, reports of hydrogen transfer to olefins are relatively scarce.[2] It has been reported that 1,4-dihydrobenzenes[2a,b] and 9(11)-dehydroergosteryl acetate[2c] are dehydrogenated by tetracyanoethylene (TCNE). However, so far as we know, the thermal hydrogen transfer from alcohols to olefins has not been reported.

During the course of the investigation of catalytic hydrogen transfer from organic compounds to olefins[3] and a quinone,[4] we found that TCNE dehydrogenates several organic compounds without catalysts. Since we were interested in the transfer of hydrogen atoms from the 1,2 positions of hydrogen donors to the 1,2 positions of hydrogen acceptors, as described later, and the preparation of derivatives of benzyl-type alcohols seemed to be relatively easy, we studied the hydrogen transfer from benzyl-type alcohols to TCNE in detail.

Results and Discussion

Hydrogen-Donating Ability. At first the susceptibility of organic compounds to dehydrogenation by TCNE was investigated under the following reaction conditons: a hydrogen donor (0.2 M) and TCNE (0.2 M) were heated at 60, 100, and 140 °C for 3 h in dioxane, which has been used as a solvent in most cases in dehydrogenation by dichlorodicyanobenzoquinone (DDQ).[1b] In addition to the dehydrogenation products anticipated, a white crystalline compound was isolated from the reaction mixtures in some cases and identified as 1,1,2,2-tetracyanoethane by comparison of melting point and IR spectrum with those of an authentic sample.[5] This fact shows that the following reaction proceeded.

$$\underset{NC}{\overset{NC}{>}}C{=}C\underset{CN}{\overset{CN}{<}} \;+\; 2H \;\longrightarrow\; \underset{CN}{\overset{CN}{\underset{|}{\overset{|}{HC}}}}{-}\underset{CN}{\overset{CN}{\underset{|}{\overset{|}{CH}}}}$$

It has been reported that TCNE undergoes substitution reactions with alcohols,[6] amines,[6,7] and aromatic compounds,[8] addition reactions with ketones,[9] and Diels–Alder reactions with dienes, including anthracene.[2a] Therefore, to obtain dehydrogenation products in good yields, the rates of the dehydrogenation reaction must be higher than those of these side reactions. If the hydrogen donors or the dehydrogenation products that form undergo side reactions, the total amount of the donors that survive and the dehydrogenation products that form becomes smaller than the amount of the donors charged. Accordingly, not only was the amount of the dehydrogenation products measured, but also the amount of the hydrogen donors that remains unreacted.

As hydrogen donors, several alcohols and hydroaromatic compounds were examined, and the results are summarized in Table I. As previously anticipated, alcohols and hydroaromatic compounds were dehydrogenated to give the corresponding carbonyl and aromatic compounds, respectively. In the reactions at 60 °C, cinnamic alcohol, 1,4-dihydronaphthalene, and 2,5-dihydrofuran were dehydrogenated considerably. In the reactions at 100 °C, the yield of dehydrogenation products decreased in the following order: cinnamic alcohol > 1,4-dihydronaphthalene > 2,5-dihydrofuran > 1,2,3,4-tetrahydroquinoline > 1-phenylethanol > 9,10-dihydroanthracene > 1-phenylpropanol > benzhydrol > benzyl alcohol > 1-phenyl-2-methylpropanol > 1,2-dihydronaphthalene. Side reactions were intensive in the reactions of benzhydrol, benzyl alcohol, and 1,2,3,4-tetrahydroquinoline and considerable in the reactions of 1-phenylethanol, cinnamic alcohol, 2,5-dihydrofuran, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene. In the reactions at 140 °C, the hydrogen-giving ability decreased in the following order: 2,5-dihydrofuran > cinnamic alcohol > 1,4-dihydronaphthalene > 9,10-dihydroanthracene > 1,2,3,4-tetrahydroquinoline > 1-phenylpropanol > 1-phenylethanol > 2-methyl-1-phenylpropanol > benzhydrol > 1,2-dihydronaphthalene > benzyl alcohol. In the reaction of 1,4-dihydronaphthalene, isomerization to 1,2-dihydronaphthalene occurred considerably. This
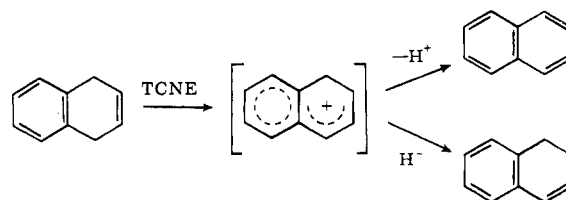
fact suggests that a carbonium ion is formed in the course of the dehydrogenation.

When 1,2-dihydro-1,1-dimethylnaphthalene was used as a hydrogen donor, rearrangement of a methyl group occurred and 1,2-dimethylnaphthalene was formed, although the yield was low. This fact also suggests that an electron deficient species was formed by the hydride abstraction at the 2 position of the hydrogen donor.

Indoline, 1-propanol, 2-propanol, and tetraline did not give the dehydrogenation products expected in the reactions at 100 and 140 °C.

Furthermore, we tried dehydrogenation by benzylidene malononitrile derivatives and fumaronitrile in reactions at 120

Table I. Dehydrogenation by TCNE [a,d]

Hydrogen donor	Registry no.	Reaction temp, °C	Yield of dehydrogenation product, %	Recovery of hydrogen donor, %
Benzyl alcohol	100-51-6	60	1	50
		100	7	52
		140	20	38
1-Phenylethanol	98-85-1	60	3	96
		100	24	64
		140	30	19
1-Phenylpropanol		60	2	95
		100	17	76
		140	34	27
2-Methyl-1-phenylpropanol	611-69-8	60	1	91
		100	6	89
		140	29	51
Benzhydrol	91-01-0	60	2	45
		100	13	26
		140	28	1
Cinnamic alcohol	104-54-1	60	24	34
		100	68	9
		140	70	0
2,5-Dihydrofuran	1708-29-8	60	7	71
		100	46	34
		140	82	4
1,4-Dihydronaphthalene	612-17-9	60	18	75[b]
		100	60	24[b]
		140	65	6[b]
1,2-Dihydronaphthalene	447-53-0	100	6	96
		140	25	67
1,2-Dihydro-1,1-dimethylnaphthalene	2733-79-1	140	5[c]	90
9,10-Dihydroanthracene	613-31-0	60	2	88
		100	24	59
		140	45	49
1,2,3,4-Tetrahydroquinoline	635-46-1	100	30	23
		140	40	15

[a] A hydrogen donor (0.2 M) and TCNE (0.2 M) were heated in dioxane for 3 h. [b] Intensive isomerization to 1,2-dihydronaphthalene was observed. [c] The dehydrogenation product was 1,2-dimethylnaphthalene. [d] Registry no.: TCNE, 670-54-2.
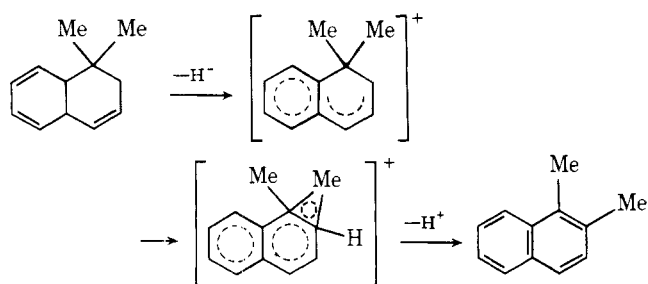
°C for 18 h in dioxane. When *m*-nitrobenzylidene malononitrile was used as a hydrogen acceptor, tetrahydroquinoline and indoline gave quinoline and indole in yields of 19 and 16% and were recovered in 72 and 43% yields, respectively. Cinnamic alcohol and 2,5-dihydrofuran formed trace amounts of cinnamaldehyde and furan, but 1-phenylpropanol and 1,2- and 1,4-dihydronaphthalenes did not undergo the dehydrogenation reaction. In the reaction of benzylidene malononitrile, indoline gave a trace (ca. 2%) of indole, but tetrahydroquinoline did not form quinoline. Both indoline and tetrahydroquinoline were not dehydrogenated by *p*-methoxybenzylidene malononitrile under the reaction conditions. These results show that electron-withdrawing substituents attached to olefinic bonds promote the dehydrogenation reaction and the hydrogen-donating power of hydroaromatic compounds

containing a nitrogen atom is strong. Fumaronitrile did not dehydrogenate even the amines described above.

As a hydrogen donor, 1-phenylpropanol and its derivatives were used in any experiment described hereafter because (1) we were interested in the hydrogen transfer from alcohols from a mechanistic viewpoint, (2) the alcohol showed a low tendency to cause side reactions and a relatively high hydrogen-giving ability, and (3) the preparation of its derivatives seemed to be easy.

Reaction Solvents. The effect of solvents was investigated to find suitable solvents and to discuss the mechanisms of the dehydrogenation reaction. Solvents that dissolved TCNE well and did not cause observable side reactions were chosen, and the results are summarized in Table II. The yield of propiophenone decreased in the following order: acetic acid > propionic acid > tetrahydrofuran > chloroform > ethyl acetate > dioxane > dichloromethane > chlorobenzene > anisole > phenetole > benzene.

Based on analogy to the dehydrogenation of hydroaromatic compounds by quinones[1] and on the fact that TCNE forms charge-transfer (CT) complexes with aromatics[10] and ethers,[10a,11] it is inferred that dehydrogenation by TCNE also occurs via the formation of CT complexes. Therefore, we speculated that the influence of solvents may be interpreted by the stabilization of the CT complexes and/or other active species, including the transition state of the reaction, by solvation. At first, we tried to identify the absorption band belonging to the TCNE/1-phenylpropanol complex in various solvents, but the bands could not be identified clearly. When toluene was used instead of the alcohol, the band due to the TCNE/toluene complex appeared at 406 nm[10a] in dichloromethane, but it overlapped with the peaks attributable to the CT complexes between TCNE and some solvents, including dioxane and tetrahydrofuran. Eventually, the relative amount of the TCNE/anisole complex was measured to estimate roughly the relative amount of the TCNE/1-phenylpropanol complex in the designated solvents. Along with the wavelength at the maximum absorption (λ_{CT}), the absorbance ($\log (I_0/I)$) is shown in Table II. The absorbance measured showed close relationship with λ_{CT}, and this fact indicates that the ease of formation of the CT complex is influenced by solvation.[12] In the reactions using solvents of similar structure, considerable correlation was observed between the yield of propiophenone and the values of the absorbance. This result suggests that the dehydrogenation reaction proceeds via the formation of CT complexes which lie before the rate-determining step of the reaction. However, the absorbance was not so closely related with the yield of the ketone in reactions in solvents of unlike structure. From this result it is assumed that solvation of other active species, perhaps the transition state of the rate-limiting step, is more important than that of the CT complex, which seems to be relatively stable.

Then we tried to correlate the yield of propiophenone to the dielectric constants of the solvents (ϵ) and the transition energy for the CT bands of pyridinium *N*-phenolbetaine (E_T) and 1-ethyl-4-carbomethoxypyridinium iodide (Z) in a given solvent.[12] These parameters are regarded as quantitative measures of ionizing power.[12] The yield of ketone seems to be explained by ϵ, E_T, and Z in a rough sense, except for the reaction in dioxane where the yield was too high and in dichloromethane where the yield was too low (Table II). The result that this hydrogen-transfer reaction proceeded more rapidly in more polar solvents suggests that the transition state of the rate-determining step is considerably charge separated. On the other hand, it is presumed that the amount of the transferred charge of the TCNE/1-phenylpropanol complex is not so large because the yield of the ketone hardly correlated with the values of ϵ, E_T, and Z of the solvents used. This presumption may be supported by the report that very little

Table II. Effect of Solvents [a]

Solvent	Yield of ketone, %	Recovery of alcohol, %	λ_{CT},[b] nm	$\log (I_0/I)$ [c]	ϵ [d]	E_T,[e] kcal mol^{-1}	Z,[f] kcal mol^{-1}
Acetic acid	28	70	480	0.32	6.2	51.9	79.2
Propionic acid	21	64	486	0.38	3.4		
Tetrahydrofuran	21	59	470	0.19	7.6	37.4	
Chloroform	18	82	512	1.2	4.8	39.1	63.2
Ethyl acetate	18	65	470	0.21	6.0	38.1	
Dioxane	14	81	460	0.15	2.2	36.0	
Dichloromethane	13	75	507	0.77	9.1	41.1	64.2
Chlorobenzene	12	76	510	1.0	5.6	37.5	
Anisole	10	83	g	g	4.3	37.2	
Phenetole	8	77	g	g	4.2		58.9
Benzene	7	90	490	0.61	2.3	34.5	54.0

[a] 1-Phenylpropanol (0.2 M) and TCNE (0.2 M) were heated at 100 °C for 2 h. [b] Wavelength of the absorption maxima of the band owing to the CT complex between TCNE (2 mM) and anisole in anisole/solvent (1:9 in volume) mixture. [c] Absorbance of the band described above. [d] Dielectric constant. [e] Molar transition energy of pyridinium N-phenolbetaine in the designated solvent.[12] [f] Same as E_T, except for the use of 1-ethyl-4-carbomethoxypyridinium iodide as the test substance.[12] [g] The absorption of the CT complex was covered by that of the solvent.

charge transfer is involved in stabilizing TCNE molecular compounds.[10b]

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

Strongly polar solvents such as N,N-dimethylacetamide, dimethyl sulfoxide, sulfolane, acetonitrile, acetone, trifluoroacetic acid, methanol, and water caused extensive side reactions, and the total amount of the propiophenone that formed and the 1-phenylpropanol that survived diminished greatly in most cases. Since all of the protonic solvents except for acetic acid and propionic acid caused side reactions, we suspected the stability of TCNE in the presence of acids. However, it was confirmed by a spectroscopic study that the amount of TCNE did not decrease when TCNE (0.1 M) and acetic acid (0.2 M) were heated at 100 °C for 1 h in dioxane.[13]

Nonpolar solvents such as n-octane, decaline, diethyl ether, and diisopropyl ether did not dissolve TCNE completely even at 100 °C.

Effect of Additives. The effect of additives was examined in a reaction in which 1-phenylpropanol (0.2 M), TCNE (0.2 M), and an additive (0.2 M) were heated at 100 °C for 2 h in dioxane, and the results are shown in Table III.

In spite of the report that dimethyl sulfoxide and N,N-dimethylacetamide react with TCNE to give anion radical species,[14] the addition of them raised the yield of propiophenone, though it caused observable side reactions. Other polar additives such as sulfolane, acetonitrile, and methanol showed no promoting effect. It has been reported that the dehydrogenation of 1,4-dihydronaphthalene by quinones is catalyzed by acids.[15] However, in our system the addition of acids showed no promoting effect.

Pyrocatechol and hydroquinone, which are inhibitors of radical reactions, did not retard the dehydrogenation reaction, and benzoylperoxide and α,α'-azobis(isobutyronitrile) (0.02 M), which are initiators of radical reactions, did not promote the reaction. This result makes it unlikely that the hydrogen-transfer reaction proceeds via a radical process,[15,16] although the result does not necessarily deny the existence of radical intermediates.

By the addition of strong bases, such as sodium acetate, pyridine, and triethylamine, the yield of ketone became negligible.

Measurement of Reaction Rates. In Figure 1 an example of the yield of propiophenone against reaction time is shown. At the initial stage of the reaction the yield of ketone was proportional to time up to about 20% in this case. The initial
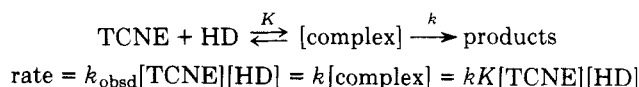
Table III. Effect of Additives [a]

Additive	Yield of ketone, %	Recovery of alcohol, %
Dimethyl sulfoxide	21	47
N,N-Dimethylacetamide	17	48
Sulfolane	14	80
Acetonitrile	13	80
Methanol	13	84
Acetic acid	14	80
Trifluoroacetic acid	13	76
Dichloroacetic acid	12	80
Pyrocatechol	14	81
Hydroquinone	12	63
Benzoyl peroxide [b]	12	70
α,α'-Azobis-(isobutyronitrile) [b]	11	68
Pyridine	1	68
Sodium acetate	1	85
Triethylamine	0	70
None	14	81

[a] 1-Phenylpropanol (0.2 M), TCNE (0.2 M), and an additive (0.2 M) were heated at 100 °C for 2 h in dioxane. [b] The amount of this additive was 0.02 M.

rate of this hydrogen-transfer reaction was derived from the linear part of the plot.

In most of the dehydrogenations by quinones, second-order kinetics has been reported.[1] In the dehydrogenation by TCNE, also, the initial rate was found to be proportional to the concentration of 1-phenylpropanol and TCNE, as shown in Figure 2. Furthermore, the fact that the proportionality was observed over a wide range of concentration of the reactants suggests that if this reaction proceeds via the formation of a complex between TCNE and the alcohol, the concentration of the complex is not to high because formation of the complex in high concentration would require deviation from the linearity shown in the plots in Figure 2.

As described previously, the rate seems to be proportional to the concentration of the CT complex in similar solvents. So the reaction scheme and rate may be expressed as follows. In these expressions, HD, K, k, and k_{obsd} represent 1-phenylpropanol, the equilibrium constant in the formation of the CT complex, the rate constant of the rate-determining step, and the observed second-order rate constant, respectively.
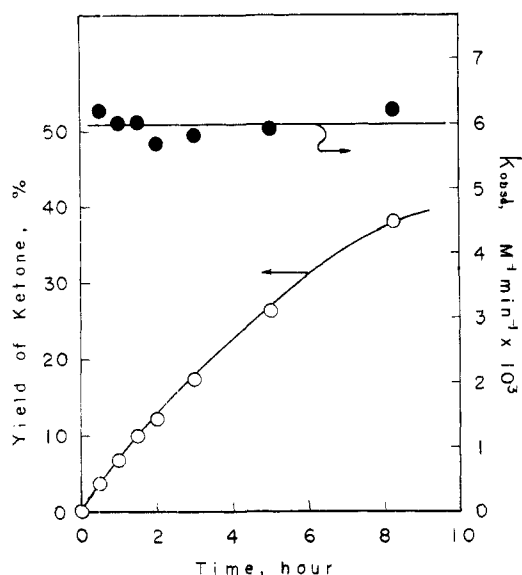
$$\text{TCNE} + \text{HD} \underset{K}{\rightleftarrows} [\text{complex}] \xrightarrow{k} \text{products}$$

$$\text{rate} = k_{obsd}[\text{TCNE}][\text{HD}] = k[\text{complex}] = kK[\text{TCNE}][\text{HD}]$$

Figure 1. Plots of the yield of ketone (O) and rate constant (●) vs. reaction time. TCNE (0.2 M) and 1-phenylpropanol (0.2 M) were heated at 100 °C in dioxane.
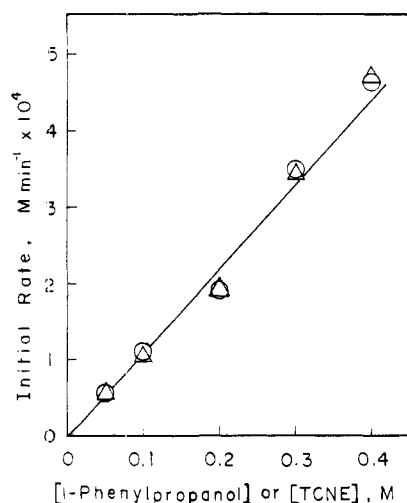

Figure 2. Plots of initial rate vs. the concentration of 1-phenylpropanol (O) and tetracyanoethylene (△); the concentration of the other reactant was 0.2 M, the temperature was 100 °C, and the solvent was dioxane.

Figure 3. Plots of log k_{obsd} vs. σ (- O -) and σ^+ (- - - △ - - -). TCNE (0.2 M) and a para- or meta- substituted 1-phenylpropanol (0.2 M) were heated in dioxane.

The values of the observed second-order rate constants were found to be almost constant up to the conversion of about 40%, as shown in Figure 1. This result indicates that side reactions are not so intensive in the initial stage of the dehydrogenation reaction.

The observed second-order rate constants were measured in dioxane at temperatures ranging from 80 to 120 °C, and a plot of the logarithm of the rate constants against the reciprocal of the reaction temperatures (K) was found to show a good linear relationship, indicating that the kinetics of the system are not to complicated. From the plot, 17.8 kcal mol⁻¹, 17.1 kcal mol⁻¹, and −31.7 eu were obtained as values for the Arrhenius energy of activation (E_a), the activation enthalpy (ΔH^*), and the activation entropy (ΔS^*) at 100 °C. The values of E_a and ΔS^* at 100 °C in the hydrogen transfer from 1,4-dihydronaphthalene to benzoquinone in phenetole, 18.9 kcal mol⁻¹ and −28.2 eu, have been reported as the values of E_a and ΔS^* at 100 °C.[15] The similarity of the values of the corresponding kinetic parameters suggests a similarity of reaction mechanism.

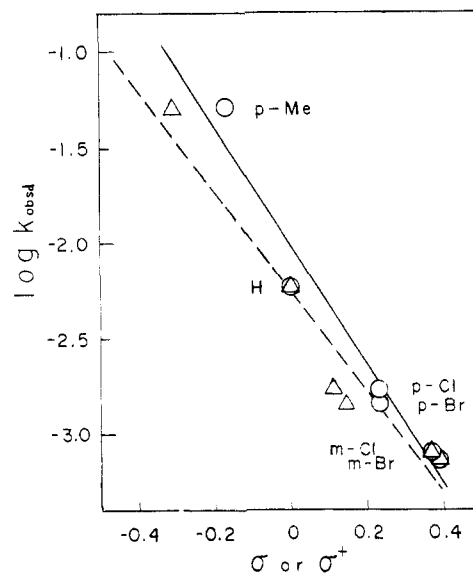**Effect of Substituents.** In a review Jackman has reported

that in the dehydrogenation of a series of 6- and 7-substituted 1,2-dihydronaphthalenes by a quinone, the rates correlate with the Hammett σ, or better still the σ^+, values of the substituents, and the observation that ρ = −2.7 is indicative of a fairly high sensitivity toward changes in substitution.[1a] Hanstein et al. have reported that the charge-transfer frequencies for complexes of TCNE with substituted benzenes correlate with σ^+ and treated the data in connection with the ability of substituents to stabilize carbonium ions.[17]
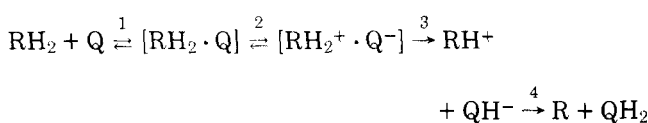
In order to discuss the electronic effect in the dehydrogenation by TCNE, p-methoxy, p-methyl, p-chloro, p-bromo, m-chloro, and m-bromo derivatives of 1-phenylpropanol were synthesized, and the second-order rate constants of the reaction of TCNE with them were measured at 100 °C in dioxane. However, in the reaction of the p-methoxy derivative, a reliable rate constant was not obtained because side reactions were remarkable.

Using the least-squares method, the logarithm of the second-order rate constants was correlated to σ to give a reaction constant of ρ of −3.13 and a correlation coefficient r of −0.976, while correlating it to σ^+ gave ρ = −2.63 and r = −0.968, as shown in Figure 3. The fairly large negative ρ values seem to show that the transition state of the rate-determining step of this reaction is much more charge separated than the species which exist before the rate-limiting step. Furthermore, these ρ values are comparable to the value reported by Jackman.[1a] The resemblance of the ρ values suggests that the reaction mechanisms of the dehydrogenation of alcohols by TCNE and that of 1,2-dihydronaphthalenes by a quinone are mutually similar.

Kinetic Isotope Effect. Müllar has reported that the rate of hydrogen transfer from 1,4-cyclohexadiene to DDQ is ten times faster than that from 1,4-cyclohexadiene-d_8 and assumed, based on the enormously large kinetic isotope effect, that cleavage of the C_1–H and C_4–H bonds occurs simultaneously in the rate-determining step.[18] Burstein and Ringold have also found that the dehydrogenation of 3α-deuterio-Δ^4-3-hydroxy steroids by DDQ was subject to a primary deuterium isotope effect (ca. fivefold).[19] However, Hashish and Hoodless obtained the result that no primary isotope effect was observed in the dehydrogenation of 1,4-dihydronaphthalene (RH₂) by tetrachlorobenzoquinone (Q) in phenetole and concluded that the rate-determining step of the reaction is not the hydrogen-transfer steps (3 and 4) but
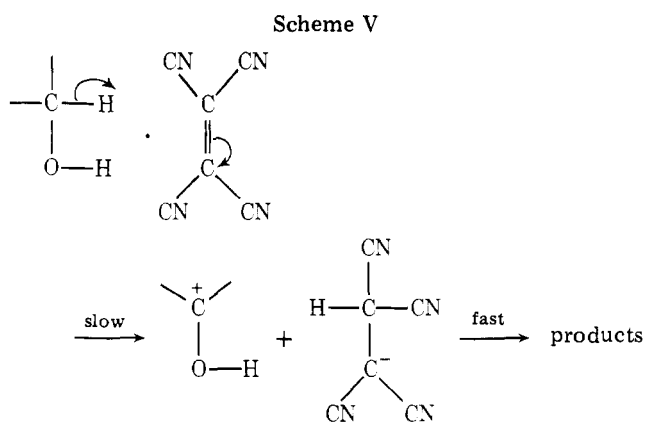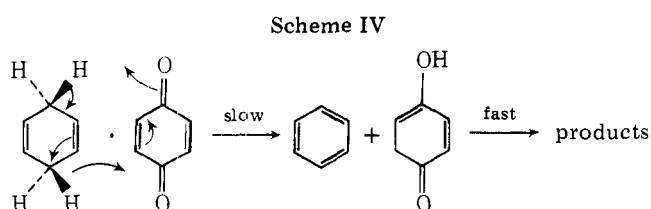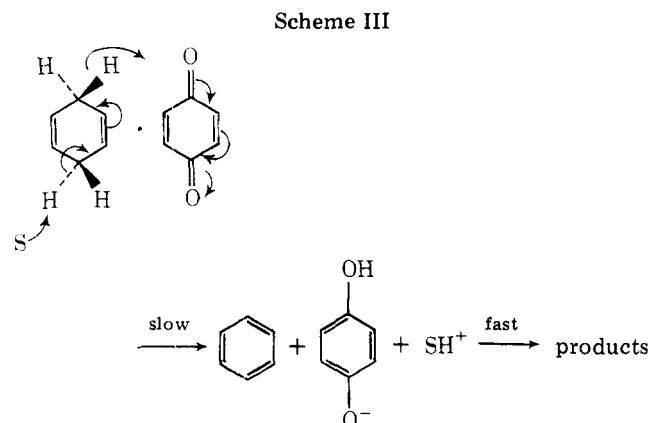
Scheme I

Scheme II
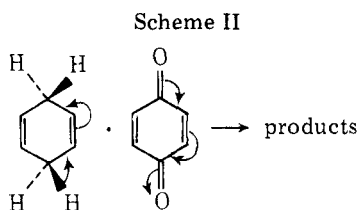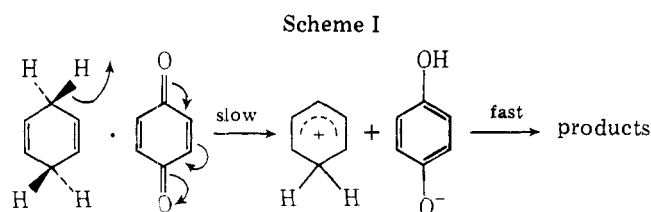
the electron-transfer step between the charge-transfer complexes (2).[28]

$$RH_2 + Q \overset{1}{\rightleftharpoons} [RH_2 \cdot Q] \overset{2}{\rightleftharpoons} [RH_2^+ \cdot Q^-] \overset{3}{\rightarrow} RH^+$$

$$+ QH^- \overset{4}{\rightarrow} R + QH_2$$

We prepared PhCD(OH)Et (CD, OH), PhCH(OD)Et (CH, OD), and PhCD(OD)Et (CD, OD), and the rates of reaction of them and PhCH(OH)Et (CH, OH) with TCNE were measured in dioxane at 100 °C. The ratios of the rates are summarized as follows: rate (CH, OH):(CD, OH) = 2.5:1; rate (CH, OD):(CD, OD) = 2.5:1; rate (CH, OH):(CH, OD) = 1.1:1; and rate (CD, OH):(CD, OD) = 1.1:1. It does not seem to be too unreasonable to consider that a primary isotope effect was observed in the transfer of the hydrogen attached to the α carbon of the alcohol while only a secondary isotope effect was observed in the transfer of the hydrogen atom of the hydroxyl group. This result suggests that cleavage of the C_α–H bond is of primary importance in the rate-determining step but that cleavage of the O–H bond is only of secondary importance or is not involved in the step.

Mechanistic Discussion. As for the dehydrogenation of 1,4-cyclohexadienes by quinones, four reaction mechanisms, as depicted below, have been proposed. Braude et al. came to the conclusion that the hydrogen transfer reaction consists of a rate-limiting hydride anion transfer from the hydrogen

Scheme III

Scheme IV

Scheme V

donors to the hydrogen acceptors, leading to a delocalized carbonium ion which loses a proton in a subsequent rapid step (Scheme I).[1a] They considered the possibility of forming benzenes in a single-step reaction (Scheme II) in which two cis hydrogen atoms are transferred to the oxygen atoms of the quinones (1,6-addition), but they rejected the concerted 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 distances of the hydrogen atoms undergoing transfer and the two quinone oxygen atoms.[20] Furthermore, they considered a mechanism involving solvents (S) as proton acceptors (Scheme III), but they rejected it also when they found that the rate of the dehydrogenation shows little dependence on the basicity of the solvents.[21] Stoos and Rocek found that the dehydrogenation with DDQ of 1,4-cyclohexadienes, which can form aromatic hydrocarbons in a one-step dehydrogenation, is about three orders of magnitude faster than that for 1,4-dienes, which cannot form aromatics in a single-step reaction, and concluded that the dehydrogenation must involve the simultaneous breaking of two carbon–hydrogen bonds.[22] They preferred 1,4-reduction of the quinone (Scheme IV), which is symmetry allowed, to 1,6-addition of hydrogen atoms to the quinone (Scheme II), which is symmetry forbidden. Later, Müller supported most strongly the concerted mechanism involving solvents (Scheme III) by comparing the rates of dehydrogenation of various hydrogen donors by DDQ.[18]

By analogy to the dehydrogenation of dihydrobenzenes by quinones, the following three reaction schemes may be considered for hydrogen transfer from alcohols to TCNE. Schemes V and VII correspond to Schemes I and III, respectively, and Scheme VI corresponds to Schemes II and IV. Scheme V, which is two-step ionic process, seems to be most reasonable because (1) a highly charge-separated transition state was required by the effect of solvents and the fairly large negative values of ρ, (2) a primary isotope effect was observed in the transfer of the hydrogen atom attached to the α carbon of 1-phenylpropanol, and (3) no phenomenon which conflicts with this scheme was observed. In this scheme the possibility of involvement of solvent in the non-rate-determining second step cannot be denied. In Scheme VI, which is a one-step cyclic process, the transfer of hydrogen is symmetry allowed because the two hydrogen atoms attached at the adjacent position of the alcohol transfer to the adjacent carbon atoms of TCNE. However, this concerted scheme does not seem to be to con-
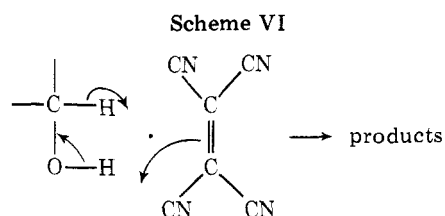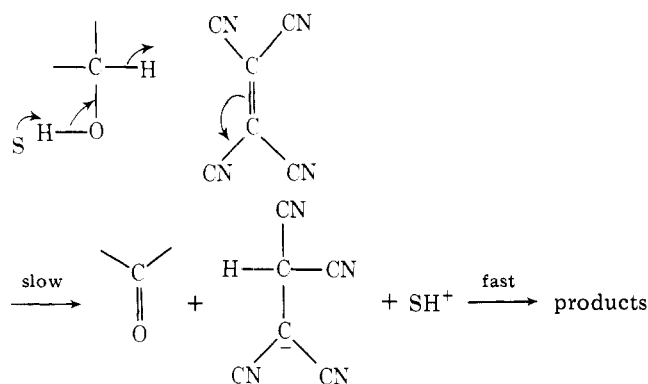
Scheme VI

<div align="center">Table IV</div>

Compd	Registry no.	τ 9.4 (CH$_3$)	τ 8.5 (CH$_2$)	τ 5.8 (CH)	τ 4.5 (OH)	τ 3.0 (Ph)
PhCH(OH)Et	93-54-91	3.2	2.0	1.1	0.9	5
PhCD(OH)Et	32047-42-0	3.0	2.2	0	1.0	5
PhCH(OD)Et	66303-46-6	3.0	1.9	1.2	0.1	5
PhCD(OD)Et	66303-45-5	3.3	2.0	0	0.3	5

Scheme VII

vincing because no primary kinetic isotope effect was observed in the transfer of the hydroxyl hydrogen of 1-phenylpropanol and the transition state is considered to be too strongly polarized for this cyclic concerted process. Scheme VII is a two-step mechanism, but the rate-limiting step is a concerted process involving a solvent as a proton acceptor. This scheme also is presumed not to be reasonable because the yield of the products of the dehydrogenation reaction was not correlated to the basicity of the reaction solvents and no primary isotope effect was observed on the transfer of the hydrogen atom of the hydroxyl group of the hydrogen donor. Furthermore, it is inferred that Scheme VII is less consistent with a highly charge-separated transition state than is Scheme V.

Experimental Section

Materials. 1,1,2,2-Tetracyanoethane,[5] 2-methyl-1-phenylpropanol,[23] 1,2-dihydro-1,1-dimethylnaphthalene,[24] and the *p*-methyl,[25] *p*-chloro-,[25] *m*-chloro,[25] *p*-bromo,[26] and *m*-bromo derivatives[27] of 1-phenylpropanol were prepared by the methods reported in the literature. All of the reagents purchased were purified by distillation or recrystallization.

Preparation of Deuterated 1-Phenylpropanols. To LiAlD$_4$ (0.4 g) in dry ether was added propiophenone dropwise with cooling by ice. The mixture was heated under reflux until the disappearance of the phenone was confirmed by GC analysis. After the addition of dilute sulfuric acid (10 mL) with cooling by ice, the organic layer was separated, washed with aqueous sodium carbonate solution and water, dried with sodium sulfate, and distilled. PhCD(OH)Et was obtained in a yield of 60%, and the boiling point at 15 mmHg was 109–112 °C.

By using deuterium oxide (10 mL) instead of dilute sulfuric acid, PhCD(OD)Et was obtained in 58% yield, and the boiling point at 15 mmHg was 93–96 °C.

To LiAlD$_4$ (1.2 g) in dry ether (40 mL) was added 1-phenylpropanol (4.0 g) dropwise with cooling by ice, and the mixture was heated under reflux for 1 h. It was cooled by ice, treated with deuterium oxide (10 mL), and heated for 1 h. Then the organic layer was separated, dried with sodium sulfate, and distilled. PhCH(OD)Et was obtained in 52% yield, and the boiling point at 18 mmHg was 109–112 °C: IR ν_{C-D} = 2100 cm^{-1} and ν_{O-D} = 2470 cm^{-1}.

Relative areas of the peaks of the 1-phenylpropanols in their ^{1}H NMR spectra, which were measured without solvent using Me$_4$Si as an internal standard, are given in Table IV.

An Example of Transfer Hydrogenation. 1-Phenylpropanol (13.8 μL, 0.1 mmol) was put into a Pyrex glass tube which had been sealed at one end. Dioxane was added, and the total volume of the solution was made to 0.5 mL. The tube was sealed under vacuum after a freeze–pump–thaw cycle at 10^{-3} Torr on a vacuum line in a liquid

nitrogen bath. The sealed tube was heated in a polyethylene glycol bath kept at 100 ± 1 °C. To analyze the reaction mixture, GC was performed at 150 °C on a Hitachi 163 instrument equipped with a flame ionization detector using 10 μL of phenylcyclohexane as an internal standard. A 1 m × 6 mm stainless steel column packed with 12% diethylene glycol succinate on Diasolid L was used. The other transfer hydrogenations were carried out in a similar way.

An Example of Kinetic Measurements. Five sealed tubes that were prepared by the method described above were heated on a polyethylene glycol bath kept at 100 ± 1 °C for 30, 60, 90, 120, and 180 min, respectively. Each reaction mixture was submitted to GC analysis. The reaction rates were obtained by the gradiation of time against the yield of ketone plot.

References and Notes

(1) (a) L. M. Jackman, *Adv. Org. Chem.*, **2**, 329 (1960); (b) D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).
(2) (a) D. T. Longone and G. L. Smith, *Tetrahedron Lett.*, 205 (1962); (b) J. Nagata, Y. Shirota, T. Nogami, and H. Mikawa, *Chem. Lett.*, 1087 (1973); (c) A. I. Andrews, R. C. Fort, and P. W. L. Quesne, *J. Org. Chem.*, **36**, 83 (1971); (d) E. A. Braude, J. Hannah, and R. P. Linstead, *J. Chem. Soc.*, 3256 (1960); (e) Y. Ohnishi, M. Kagami, T. Numakunai, and A. Ohno, *Chem. Lett.*, 915 (1976); (f) K. Wallenfels, W. Ertel, and K. Friedrich, *Justus Liebigs Ann. Chem.*, 1663 (1973); (g) K. Nanjo, K. Suzuki, and M. Sekiya, *Chem. Lett.*, 1169 (1976).
(3) (a) T. Nishiguchi and K. Fukuzumi, *J. Am. Chem. Soc.*, **96**, 1893 (1974); (b) H. Imai, T. Nishiguchi, and K. Fukuzumi, *J. Org. Chem.*, **39**, 1622 (1974); (c) T. Nishiguchi, K. Tachi, and K. Fukuzumi, *ibid.*, **40**, 237, 240 (1975); (d) H. Imai, T. Nishiguchi, M. Kobayashi, and K. Fukuzumi, *Bull. Chem. Soc. Jpn.*, **48**, 1585 (1975); (e) T. Nishiguchi, H. Imai, Y. Hirose, and K. Fukuzumi, *J. Catal.*, **41**, 249 (1976); (f) T. Nishiguchi, H. Imai, T. Tagawa, and K. Fukuzumi, *J. Am. Oil Chem. Soc.*, **54**, 144 (1977).
(4) T. Nishiguchi, A. Kurooka, and K. Fukuzumi, *J. Org. Chem.*, **39**, 2403 (1974).
(5) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Crespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).
(6) W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2780 (1958).
(7) (a) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958); (b) Z. Rappoport and E. Shohamy, *Isr. J. Chem.*, **6**, 865 (1968); *Chem Abstr.*, **71**, 331 (1969).
(8) G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2518 (1958).
(9) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).
(10) (a) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958); (b) W. C. Herndon and R. D. Goodin, *J. Phys. Chem.*, **73**, 2793 (1969); (c) H. Sakurai, *J. Org. Chem.*, **35**, 2807 (1970).
(11) (a) R. Vars, L. A. Tripp, and L. W. Pickett, *J. Phys. Chem.*, **66**, 1754 (1962); (b) Y. Achiba, S. Katsumata, and K. Kimura, *Bull. Chem. Soc. Jpn.*, **45**, 1272 (1972).
(12) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).
(13) When TCNE (0.2 M) was heated in acetic acid, the absorption of TCNE in the UV spectrum was covered by the strong absorptions of the acid.
(14) N. Kushibiki and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **50**, 349 (1977).
(15) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548 (1954).
(16) J. B. Bradley, D. E. Conner, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Am. Chem. Soc.*, **94**, 4043 (1972)
(17) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970).
(18) P. Müller, *Helv. Chim. Acta*, **56**, 1243 (1973).
(19) S. H. Burstein and H. J. Ringold, *J. Am. Chem. Soc.*, **86**, 4952 (1964).
(20) E. A. Braude, L. M. Jackman, R. P. Linstead, and J. S. Shannon, *J. Chem. Soc.*, 3116 (1960).
(21) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3564 (1954).
(22) F. Stoos and J. Rocek, *J. Am. Chem. Soc.*, **94**, 2719 (1972).
(23) J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, **50**, 554 (1928).
(24) E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe *J. Chem. Soc.*, 3133 (1960).
(25) C. Bocard, M. Davidson, M. Hellin, and F. Cossemant, *Bull. Soc. Chim. Fr.*, 163 (1971).
(26) J. Seyden-Penne and C. Schaal, *Bull. Soc. Chim. Fr.*, 3653 (1969).
(27) J. Frejka and H. Zámiš, *Cas. Cesk. Lek.*, **63**, 157 (1950); *Chem. Abstr.*, **47**, 2131e (1953).
(28) Z. M. Hashish and I. M. Hoodless, *Can. J. Chem.*, **54**, 2261 (1976).