KINETICS OF HYDROGEN ABSTRACTION FROM PROTON DONORS BY DPPH[1]

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ABSTRACT

The kinetics and energetics of the interaction of DPPH with a variety of hydroxylic compounds have been investigated by electronic and e.s.r. spectroscopy. Deuterium isotope effects on the kinetics have been examined. A model involving hydrogen bonded complexes has been suggested for the hydrogen abstraction reaction.

INTRODUCTION

The interaction of DPPH with proton donors has been investigated by several workers (1–6) in recent years, although there is limited information on the energetics of the reaction. While it was believed earlier (2) that the interaction of proton donors with DPPH involved hydride ion transfer and formation of carbonium ions, recent work of Russell and co-workers (3, 4, 6) has shown that this reaction involves the formation of radicals by hydrogen abstraction from a hydrogen bonded complex initially formed between the proton donors and DPPH. Thus, Russell and coworkers (6) have identified the formation of the stable 2,4,6-tri-*t*-butylphenoxy radical in the interaction of 2,4,6-tri-*t*-butylphenol with DPPH by electron spin resonance (e.s.r.) spectroscopy.

We have now investigated the kinetics and energetics of the interaction of DPPH with a variety of proton donors: (i) substituted phenols with varying basicity, (ii) sterically hindered phenols, (iii) 4-substituted-2,6-di-*t*-butylphenols, (iv) sterically hindered alcohols, (v) ortho-substituted (intramolecularly hydrogen bonded) phenols, and (vi) aniline and aniline-d_2, phenol and phenol-*d*, and oxalic acid and oxalic acid-d_2.

In addition to providing useful kinetic information, these studies were expected to throw some light on the nature of the hydrogen bonded complexes which act as intermediates or activated complexes in the hydrogen abstraction reaction.

EXPERIMENTAL

DPPH was prepared by the lead oxide oxidation of diphenyl picryl hydrazine. 2,2,4,4-Tetramethyl-3-isopropyl-3-pentanol was prepared by the method described in the literature (7). Deuterated compounds were obtained from the Atomic Energy Establishment, Bombay. All the other chemicals used were obtained commercially and were purified before use.

DPPH gives violet colored solutions in organic solvents and is stable up to about 80 °C. The solutions show an absorption maximum around 520 mμ with an extinction coefficient of ~12 000 l mole^{-1} cm^{-1}. Another high intensity absorption maximum appears at ~330 mμ. The 520 mμ band was used to determine the concentration of DPPH in the kinetic studies of the interaction of DPPH with proton donors.

The measurements of electronic spectra were made with a Beckman DU spectrophotometer, fitted with a variable temperature cell compartment. The pseudo-first order kinetics of interaction of DPPH with proton donors were followed (for less than the first 30–40% of the reaction) in carbon tetrachloride solutions in the presence of excess of proton donors. The concentration of DPPH was generally ~$10^{-5}M$ while that of proton donors varied between ~10^{-4} and ~$0.1M$. The rate constants for the second order reactions were then calculated employing an expression similar to that of McGowan, Powell, and Raw (2).

$$k_{II} = \frac{2.303}{t} \log \frac{a}{a-x} \times \frac{1}{D}$$

$$= \frac{2.303}{t} \log \frac{D_0}{D_t} \times \frac{1}{D}$$

[1]*Taken in part from the Ph.D. Thesis of S. Singh submitted to the Indian Institute of Technology, Kanpur.*
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where a and $(a - x)$ are the initial and final molar concentrations of DPPH after t minutes when D moles of proton donor has been allowed to react with it. Typical plots of log D_t against time are shown in Fig. 1.

The rate constants were also calculated by noting the rate of disappearance (decrease in the peak height of the first derivative curve) of the electron spin resonance signal of DPPH with time. Generally, there was no interference in the e.s.r. spectrum due to the phenoxy or other radicals, except in the case of 2,4,6-tri-*t*-butylphenoxy radical (6). Since the kinetics in such cases were also examined by electronic spectroscopy, there was no difficulty in obtaining good rate constants. Typical e.s.r. signals of DPPH as a function of time in presence of phenol are shown in Fig. 2. A Varian H-4500 spectrometer operating at 100 kc/s was employed for this purpose.

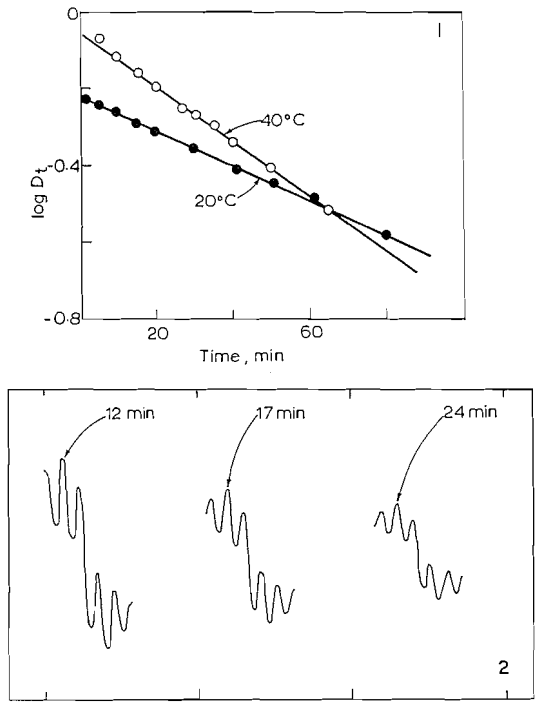

FIG. 1. Typical first order plots for the reaction of DPPH with 2,6-di-*t*-butylphenol at two temperatures.
FIG. 2. Time dependence of the e.s.r. signal of DPPH ($\sim 10^{-4}$ M) in the presence of phenol (~ 0.05 M, solvent CCl_4).

The rate constants have an uncertainty less than $\pm 10\%$. Reverse reactions of phenoxy and other radicals do not affect the k values appreciably since the proton donors were present in excess and since the rate data were taken only for the initial few percent of the reaction. Rate constants were determined at three temperatures in the 20–40 °C range and the energy of activation was calculated using the Arrhenius equation. Rate constants at only one temperature have been shown in the tables for purpose of brevity. The uncertainty in the energy of activation is ± 1 kcal mole^{-1}.

The hydrogen bonding data given in Tables I–VI are from the studies in this laboratory (7, 8).

RESULTS AND DISCUSSION

The interaction of a proton donor, RXH, with DPPH may be visualized to proceed as follows. (i) The RXH first forms a hydrogen bonded complex, X—H...N, with DPPH. (ii) the hydrogen of this complex is then transferred completely to the nitrogen atom forming the hydrazine and a radical, through a transition state where the X—H bond is more polarized than in the initial hydrogen bonded complex. Such an activated complex may be considered to be similar to the symmetrical hydrogen bond X...H...N. (iii) The facility with which the hydrogen abstraction takes place is determined by several factors. A low free energy of formation (ΔF^0) of the initial hydrogen bonded complex should

increase the rate constant since the rate will be proportional to the concentration of the hydrogen bonded species. Strong hydrogen bonds (high enthalpy of formation of the complex, $-\Delta H^0$) should lower the energy of activation, E_a, for the hydrogen abstraction reaction since a stronger hydrogen bond will approximate a symmetrical hydrogen bond more closely. The stability of the radical produced by hydrogen abstraction should also favor the hydrogen abstraction due to obvious thermodynamic reasons. All these ideas regarding the hydrogen abstraction reaction between DPPH and proton donors have been summarized in the form of a potential energy diagram in Fig. 3. In the present discussion the reverse reaction of the phenoxy or other radicals with the hydrazine (6) will not be considered, and the rate data presented are only for the forward reaction of DPPH with the proton donors.

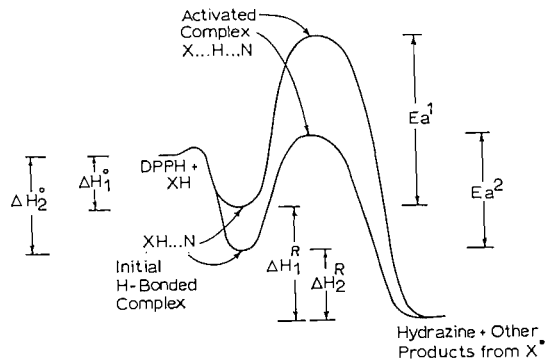

FIG. 3. Potential energy diagram for the interaction of DPPH with proton donors. DPPH and a proton donor XH initially form a hydrogen bonded complex XH...N which then forms an activated complex, X...H...N ($R_{X...H} > R_{X-H}$) resembling a symmetric hydrogen bond. Two cases have been considered, one with a high and another with a medium value for the enthalpy of formation ($-\Delta H^\circ$)of the initial hydrogen bonded complex. The energy levels of the hydrazine and other products formed by the new radicals are shown to be the same for both cases for the purpose of simplicity. ΔH^R is the enthalpy change for the reaction giving rise to the hydrazine and the products from X•.

From these arguments it is clear that one should not expect a simple relationship between the data on hydrogen bonding and the kinetics of hydrogen abstraction. However, in certain systems, one may see some relation between the ΔH^0 (also $\Delta\nu_{OH}$) and ΔF^0 of hydrogen bonding and the energy of activation. In systems where the radicals produced have nearly the same stabilities, it is possible that ΔH^0 of hydrogen bonding as well as $\Delta\nu_{OH}$ may be inversely proportional to the energy of activation for hydrogen abstraction.

Interaction of DPPH with p-Substituted Phenols

The kinetic data for the interaction of DPPH with *p*-substituted phenols are given in Table I. It can be seen that there is no simple relationship between the rate constant or the energy of activation and the electrical properties of the *p*-substituents. This is probably due to the operation of several of the factors discussed earlier. Comparison of these kinetic data with the hydrogen bonding data of these proton donors with benzophenone, however, shows that *p*-chlorophenol which forms the strongest hydrogen bond (being the most acidic of the four phenols studied) does not show the lowest value of the energy of activation.

Interaction of DPPH with Sterically Hindered Phenols and Alcohols

The data for the interaction of DPPH with sterically hindered phenols are given in Table II. Although there is no simple relationship between the rate constants or the energies of activation with the bulk of the ortho substituents, it can be seen that the

TABLE I

Interaction of substituted phenols (RC_6H_4OH) with DPPH

R	σ (9)	$k_{20°C}$,* min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.	Benzophenone hydrogen bonding (8) $K_{25°C}$, l $mole^{-1}$	$\Delta\nu_{OH}$, cm^{-1}	$-\Delta H^0$, kcal $mole^{-1}$
4-Cl†	0.23	5.5 (5.6)	6.5	43	14	190	4.9
H‡	0.00	2.9 (2.7)	6.9	45	7.7	175	4.4
4-CH_3 (2)	−0.17	55.0	9.8	27	6.3	160	—
4-OCH_3§	−0.27	3 350 (3 860)	6.5	31	7.3	170	4.4

*Values of k in parentheses are from e.s.r. measurements.
†k from ref. 2 is 1.1 at 20 °C.
‡k from ref. 2 is 4.0 at 20 °C.
§The reaction was not pseudo-first order in this case since the concentration of the phenol and DPPH were nearly the same. The value found by other workers (2) is 14 000 which is very high because they calculated k treating the reaction as pseudo-first order.

TABLE II

Interaction of sterically hindered phenols ($R_1R_2C_6H_3OH$) with DPPH*

R_1	R_2	$k_{20°C}$, min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.	THF hydrogen bonding (7) $K_{25°C}$, l $mole^{-1}$	$-\Delta H^0$, kcal $mole^{-1}$
H	2-*t*-Bu	36	6.4	39	7	5
2-Me	6-Me†	82 (83)	7.0	36	2.5	—
2-*i*-Pr	6-*i*-Pr	79 (81)	11	22	1.8	5
2-*t*-Bu	6-*t*-Bu‡	15 (19)	3.7	50	0.5	8

*Values of k in parentheses are from e.s.r. measurements.
†The k at 20 °C from ref. 2 is 117.
‡The k at 30 °C from ref. 4 is 1.2 and from ref. 2 is 12.0.

2,6-di-*t*-butylphenol which forms the strongest hydrogen bond (high $-\Delta H^0$) shows the lowest energy of activation for hydrogen abstraction. The rate constant, however, is low in this case probably due to the very low equilibrium constant of formation of the hydrogen bonded complex.

The kinetics of hydrogen abstraction of a sterically hindered alcohol with DPPH are compared in Table III with the data on ethanol.

Although the reaction of ethanol gives complex products, one can treat the reaction as of pseudo-first order. The value of k has been given here only to show the large difference

TABLE III

Interaction of aliphatic alcohols with DPPH

	$k_{25°C}$, min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.	Benzophenone hydrogen bonding $K_{25°C}$, l $mole^{-1}$	$10^{-3}\Delta\nu/\nu$
2,2,4,4-Tetramethyl-3-isopropyl-3-pentanol	3×10^{-3}	20	13	0.6	17.1
Ethanol (5)	4×10^{-10}	9.6	79	1.9	23.6

in rates between the two alcohols. The sterically hindered alcohol shows a much faster rate. The energy of activation is high possibly because of a lower enthalpy of formation of the hydrogen bonded complex.

It has been found earlier that there was no systematic variation of the equilibrium constant or the $\Delta\nu_{OH}$ in the hydrogen bonding equilibrium of *p*-substituted 2,6-di-*t*-butylphenols with donors (7). It is interesting to see, however, that the energy of activation of hydrogen abstraction varies roughly in the same fashion as the $\Delta\nu_{OH}$ (Table IV). 2,4,6-Tri-*t*-butylphenol is slightly out of line and the value of the energy of activation is not as low as one would have expected.

TABLE IV

Interaction of *p*-substituted (R) 2,6-di-*t*-butylphenols with DPPH

					THF hydrogen bonding (7)	
4-R	σ (10)	$k_{20°C}$, min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.	$K_{25°C}$ l $mole^{-1}$	$10^3\Delta\nu/\nu$
NO_2	1.24	1.3	8.6	39	1.3	27.6
CN	0.88	9.6	11	27	1.3	28.9
COOEt*	0.64	15	6.9	39	1.1	26.1
H	0.00	15	3.7	50	0.5	23.0
t-Bu (6)	−0.14	7.2	6.5	42	0.5	22.0

*The rate constant determined by e.s.r. was 16 min^{-1}.

TABLE V

Interaction of intramolecularly hydrogen bonded phenols $R_1R_2C_6H_3OH$ with DPPH

R_1	R_2	$k_{20°C}$, min^{-1}	E_a kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.
H	2-Cl	0.21	11	32
2-Cl	6-Cl	2.2	7	44
2-Br	6-Br	1.5	4	54
H	2-$COCH_3$	0.02	8	49
H	2-NO_2*	0.002	3	69

*The rate constant determined by e.s.r. was found to be 0.003 min^{-1}.

Interaction of DPPH with Intramolecularly Hydrogen Bonded ortho-Substituted Phenols

Studies on the intramolecularly hydrogen bonded ortho-substituted phenols show that hydrogen can be abstracted from even the stronger intramolecular hydrogen bonds (Table V). 2,6-Dichlorophenol which can exist only in the bonded *cis* form, shows a much lower rate constant as well as energy of activation for hydrogen abstraction compared with ortho-chlorophenol which can exist either in the *cis* (hydrogen bonded) or the *trans* form. It appears as though the E_a decreases with an increase in the energy of the intramolecular hydrogen bond. 2-Nitrophenol which probably has the strongest intramolecular hydrogen bond also shows the lowest value of E_a. It is possible that in the case of 2-nitrophenol, it forms the strongest intermolecular hydrogen bond with DPPH as well. The low rate constant, however, is likely to be due to the low concentration of the hydrogen bonded species with DPPH since it will be more difficult to break a strong intramolecular hydrogen bond.

Deuterium Isotope Effects on the Hydrogen Abstraction Reaction

The results in Table VI clearly show that deuterium substitution lowers the rate constant for hydrogen abstraction and increases the E_a considerably. The k_H/k_D ratio varies

anywhere between 1 and 12. The lowering of the rate constant by deuterium substitution can be understood in terms of the kinetic isotope effects discussed in the literature (11). It is interesting to note that the equilibrium constants and enthalpies of formation of intermolecular hydrogen bonds are also considerably decreased by deuterium substitution (12).

TABLE VI

Deuterium isotope effects*

	X—H			X—D		
	$k_{20°C}$, min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.	$k_{20°C}$, min^{-1}	E_a, kcal $mole^{-1}$	$-\Delta S^{\neq}$, e.u.
Phenol	2.9	6.1	45	2.1	8.9	40
2,4,6-Tri-*t*-butylphenol (6)	7.2	6.5	42	0.60	7.7	43
Aniline†	0.06	6.6	51	0.04	13	29
Oxalic acid‡	0.19	9.4	40	0.10	2.5	64

*CCl_4 was used throughout as the solvent except in the case of oxalic acid where CH_3CN was used.
†McGowan, Powell, and Raw (2) have treated the reaction of primary amines with DPPH as a third order reaction. In the present study it has been found that better fits of the rate data are obtained if the reaction is treated as second order.
‡In oxalic acid there is the possibility of formation of a diradical which would mean a third order reaction. Here, values have been calculated assuming a second order reaction only.

Entropy of Activation of the Hydrogen Abstraction Reaction

In all the systems examined in the present study, the entropies of activation for hydrogen abstraction calculated from the Eyring equation (11) are large negative numbers. This appears reasonable since the activated complex (symmetric hydrogen bond) is more polar than the initial hydrogen bond complex between the proton donor and DPPH (Fig. 3).

CONCLUDING REMARKS

Although the hydrogen abstraction reaction of DPPH with proton donors seems to be fairly well understood (3–6), the detailed mechanism of the interaction is difficult to establish from kinetic studies alone. While it is possible to visualize a plausible mechanism (Fig. 3), the kinetics in most instances seem to be affected by more than one factor. In some instances, however, it is possible to show some relation between the kinetic data and the hydrogen bonding data.

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