192 J. Org. Chem. 1993, 58, 192-196

Solvent Effects in the Hydrogen Abstractions by *tert*-Butoxy Radical: Veracity of the Reactivity/Selectivity Principle[†,1]

Sung Soo Kim,* Sung Yeon Kim, Seung Sin Ryou, Choon Seung Lee, and Kwang Hee Yoo

Department of Chemistry, Inha University, Incheon 402-751, South Korea

Received January 9, 1992 (Revised Manuscript Received August 4, 1992)

The Hammett correlations and primary deuterium kinetic isotope effects were obtained to investigate the solvent effects on hydrogen abstractions from thiophenols, phenols, and toluenes by *tert*-butoxy radical, where the latter proved to be a more sensitive probe than the former. The limitations of the reactivity/selectivity principle are discussed in terms of either anti-Hammond effects or Marcus theory and attributed to the duality in substituent (solvent) effects, that is thermodynamic substituent (solvent) effects differing from kinetic substituent (solvent) effects. While the polar transition states for the homolytic reactions should invite dual substituent effects, the dual solvations of *tert*-butoxy radical could trigger the dualism of solvent effects. The influence on the rates in general may dwindle in the order of structure > substituent > solvent.

tert-Butoxy radical[2] can engender solvations with appropriate solvent molecules which had been well investigated for hydrogen abstractions from cyclohexane and 2,3-dimethylbutane (DMB). Variations of the ratio for rate of abstraction vs that of β-scission, i.e. k_a/k_d, were examined with regard to changes of solvent and temperature, and it was shown that dipolar interactions were mainly responsible for the reduction of reactivity of *tert*-butoxy radical. Chlorine atom[3] may, on the other hand, enjoy π-complexation with electron-rich molecules to invite remarkable decrease in reactivity. The relative rates for tertiary H to primary H abstractions from DMB, i.e., k_t/k_p, could be termed as selectivity, which appears much greater for solvent-free *tert*-butoxy radical[2] with k_t/k_p = 44 at 40 °C than for equivalent chlorine atom[3] with k_t/k_p = 3.9 at 40 °C. The values of k_t/k_p for both radicals[2,3] tend normally to be larger with stronger solvation according to the oft-cited reactivity/selectvity principle (RSP).[4] When "relative k_t/k_p" could be defined by setting k_t/k_p = 1 for the reactions free of solvent effects, the solvations accordingly boost "relative k_t/k_p" to become greater than unity.[2,3] In several highly polar media, the reactions of *tert*-butoxy radical, however, to our surprise, disclosed "relative k_t/k_p" < 1, which must violate[5] the rule of RSP. Such peculiar reductions of selectivity were caused by serious decrease in logarithms of ratios of preexponential factors for abstractions of primary and tertiary hydrogen atoms in DMB, that is log (A_t/A_p), which is then closely related with differential entropies of activation between the two different hydrogen abstractions as follows 2.303 log $(A_t/A_p) = (\Delta S^{\ddagger}_t - \Delta S^{\ddagger}_p)/R$, a phenomenon reminiscent of entropy control of selectivity boasting of non-RSP behavior with polar transition state (TS).[6-9] *tert*-Butoxy radical abstracted hydrogens from phenols[10] to exhibit quite unidentical Hammett correlations with different solvents, that is $\rho^+ = -1.19$ (CCl_4) and $\rho^+ = -0.79$ (C_6H_5Cl), both at 122 °C. Since ρ^+ can be also taken as a selectivity parameter, the solvation with C_6H_5Cl renders *tert*-butoxy radical to carry less reactivity and selectivity than in the case of CCl_4, which again denies the well-known inverse relationship.[4] The failures[5] of RSP have been relatively well investigated for the polar reactions and rationalized in terms of anti-Hammond effects.[11-13] The homolytic fragmentations of carbinyloxy radicals[14] could be the first example of homolytic reactions defying the authority of RSP[4] with temperature change, which has been explained by the Marcus theory.[15]

We introduce novel aspects of solvent contribution to the reactivities for the hydrogen abstractions by *tert*-butoxy radical derived from *tert*-butyl peroxide employing the reactions shown in Scheme I.

Scheme I

$$t\text{-BuO}^{\bullet} \xrightarrow{k_d} CH_3^{\bullet} + CH_3COCH_3 \qquad (1)$$

$$YC_6H_4X\text{–}H + t\text{-BuO}^{\bullet} \xrightarrow{k_Y} YC_6H_4X^{\bullet} + t\text{-BuOH} \qquad (2)$$

$$C_6H_5X\text{–}H(D) + t\text{-BuO}^{\bullet} \xrightarrow{k_{H(D)}} C_6H_5X^{\bullet} + t\text{-BuOH(D)} \qquad (3)$$

$$X = O \text{ and } S$$

Results and Discussion

Determinations of Relative Rates, Hammett Correlations, and Primary Deuterium Kinetic Isotope

---

[†] Dedicated to professor Cheves Walling.

(1) Presented at the 3rd European Symposium on Organic Reactivity, Göteborg, Sweden, July 7-12, 1991.

(2) (a) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1962**, *84*, 2845. (b) Walling, C.; Wagner, P. *J. Am. Chem. Soc.* **1963**, *85*, 2333. (c) *Ibid.* **1964**, *86*, 3368. (d) *Ibid.* **1965**, *87*, 5179.

(3) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987.

(4) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963.

(5) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (b) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755. (c) Pross, A. *Adv. Phy. Org. Chem.* **1977**, *14*, 69. (d) McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331. (e) The whole volume of *Isr. J. Chem.* **1985**, *26*, 303-427. (f) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511. (g) Buncel, E.; Wilson, H. *J. Chem. Educ.* **1987**, *64*, 476.

(6) Kim, S. S.; Choi, S. Y.; Kang, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 4234.

(7) (a) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* 1981, *103*, 4162. (b) We calculated ρ^+ from Table III of the above reference, which are $\rho^+ = -0.88$ (22 °C), -0.68 (0 °C), -0.62 (-30 °C), and -0.48 (-60 °C) in $C_6H_5CH_3$.

(8) Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438.

(9) (a) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028. (b) Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685.

(10) Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2816.

(11) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225.

(12) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

(13) More O'Ferall, R. A. *J. Chem. Soc.* B **1970**, 274.

(14) Kim, S. S.; Kim, C. J.; Youn, S. J.; Ra, H. S.; Lee, J. C. *Tetrahedron Lett.* **1991**, *32*, 4725.

(15) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

0022-3263/93/1958-0192$04.00/0

Table I. Relative Reactivities of YC_6H_4SH toward *tert*-Butoxy Radical and Hammett Correlations at 130 °C

$$YC_6H_4SH + t\text{-}BuO^\bullet \xrightarrow{k_Y} YC_6H_4S^\bullet + t\text{-}BuOH;\ C_6H_5SH + t\text{-}BuO^\bullet \xrightarrow{k_H} C_6H_5S^\bullet + t\text{-}BuOH$$

	k_Y/k_H;[a] Y =						Hammett correlations	
solvents	*p*-OCH_3	*p*-CH_3	*p*-F	H	*p*-Cl	*p*-Br	ρ^{+b} $(r)^c$	ρ^b $(r)^c$
CCl_4[d,e]	1.76	1.30	1.18	1	1.01	0.92	−0.30 (0.985)	−0.49 (0.889)
C_6H_6[d,e]	1.74	1.25	0.98	1	1.07	0.87	−0.30 (0.987)	−0.44 (0.850)
CS_2 (2 M)/CCl_4[d,e]	1.79	1.26	1.18	1	1.07	0.87	−0.29 (0.960)	−0.44 (0.848)
CH_3CO_2H[f]	(18.1)	(12.9)	(11.7)	(10.9)	(10.2)		−0.27 (0.996)	−0.44 (0.883)

[a] Error limits are less than 3%, being average deviations of more than three runs. [b] Plotted against σ^+ for ρ^+ and σ for ρ. [c] Correlation coefficients. [d] The rates were obtained via direct competitions.[2,16] [e] Control experiments indicated that exchange reactions, i.e. $YC_6H_4SH = C_6H_5S^\bullet \rightleftharpoons YC_6H_4S^\bullet = C_6H_5SH$, should be negligible not to alter the rates. [f] The rates were determined by indirect method[2,17] and the figures in parentheses accordingly correspond to k_Y/k_d.

Table II. Relative Reactivities of YC_6H_4OH toward *tert*-Butoxy Radical and Hammett Correlation at 130 °C

$$YC_6H_4OH + t\text{-}BuO^\bullet \xrightarrow{k_Y} YC_6H_4O^\bullet + t\text{-}BuOH;\ C_6H_5OH + t\text{-}BuO^\bullet \xrightarrow{k_H} C_6H_5O^\bullet + t\text{-}BuOH$$

	k_Y/k_H;[a,b] Y =				Hammett correlations	
solvent	*p*-OCH_3	*p*-CH_3	H	*p*-Cl	ρ^{+c} $(r)^d$	ρ^c $(r)^d$
CCl_4	29.65	6.24	1	0.85	−1.81 (0.990)	−3.01 (0.905)
C_6H_6	13.98	3.62	1	0.73	−1.46 (0.996)	−2.46 (0.919)
CH_3CN	5.86	2.02	1	0.69	−1.02 (0.999)	−1.73 (0.926)

[a] The rates were determined by direct competitions[2,16] with error limits far less than 3% which were average deviations of three runs. [b] Control experiments indicated that exchange reactions, i.e. $YC_6H_4OH = C_6H_5O^\bullet \rightleftharpoons YC_6H_4O^\bullet = C_6H_5OH$, should be insignificant not to alter the rates. [c] Plotted against σ^+ for ρ^+ and σ for ρ. [d] Correlation coefficients.

Effects. The relative rates of hydrogen abstractions from YC_6H_4SH by *tert*-butoxy radical in CCl_4, C_6H_6, and CS_2 (2 M)/CCl_4 were obtained with C_6H_5SH as a standard substrate using

$$k_Y/k_H = \log\,(Y_f/Y_i)/\log\,(H_f/H_i) \qquad (4)$$

where Y and H represent respectively molar concentrations of YC_6H_4SH and C_6H_5SH with subscripts f and i standing for final and initial, respectively (direct competition).[2,16] The same reactivities in CH_3CO_2H could be derived from

$$k_Y/k_d = ([t\text{-}BuOH]/[CH_3COCH_3])\cdot 1/[YC_6H_4SH] \qquad (5)$$

where β-scission of *tert*-butoxy radical was used as a reference reaction (indirect competition).[2,17] The fragmentation could become competitive with the hydrogen abstraction in CH_3CO_2H because H-bonding between *tert*-butoxy radical and CH_3CO_2H may slow down the rate of abstraction which appears otherwise[7] close to diffusion control limit. The alternative method[16,17] thus afforded relative rates as either k_Y/k_H or k_Y/k_d wherefrom the Hammett correlations could be derived (Table I). The relative rates for reactions of YC_6H_4OH in CCl_4, C_6H_6, and CH_3CN were similarly measured by direct competition[2,16] with eq 4 where phenols however replaced thiophenols. The rates and Hammett correlations are given in Table II. The primary deuterium kinetic isotope effects (PDKIE)[18] were evaluated for three pairs of substrates, i.e. C_6H_5OH/C_6H_5OD, C_6H_5SH/C_6H_5SD, and $C_6H_5CH_3/C_6D_5CD_3$ (Table III). The k_H/k_D for

$$C_6H_5X\text{–}H(D) + t\text{-}BuO^\bullet \xrightarrow{k_{H(D)}} C_6H_5X^\bullet + t\text{-}BuOH(D)$$

with X = O and S, could be obtained as

$$k_H/k_D = (k_H/k_{p\text{-}Br})(k_{p\text{-}Br}/k_D) \qquad (6a)$$

when X = O and

$$k_H/k_D = (k_H/k_{p\text{-}Cl})(k_{p\text{-}Cl}/k_D) \qquad (6b)$$

when X = S, where

$$p\text{-}BrC_6H_4OH + t\text{-}BuO^\bullet \xrightarrow{k_{p\text{-}Br}} p\text{-}BrC_6H_4O^\bullet + t\text{-}BuOH \text{ and}$$

$$p\text{-}ClC_6H_4SH + t\text{-}BuO^\bullet \xrightarrow{k_{p\text{-}Cl}} p\text{-}ClC_6H_4S^\bullet + t\text{-}BuOH$$

The values of $k_H/k_{p\text{-}Br}$ and $k_D/k_{p\text{-}Br}$ were then available from direct competition method[16] with pairs of C_6H_5OH/*p*-BrC_6H_4OH and C_6H_5OD/*p*-BrC_6H_4OH, respectively. Similar procedures provided figures for $k_H/k_{p\text{-}Cl}$ and $k_D/k_{p\text{-}Cl}$ from the competitions of C_6H_5SH/*p*-ClC_6H_4SH and C_6H_5SD/*p*-ClC_6H_4SH, respectively. The PDKIE were calculated from

$$k_H/k_D = (k_H/k_d)(k_d/k_D) \qquad (7)$$

for

$$C_6H_5CH_3 + t\text{-}BuO^\bullet \xrightarrow{k_H} C_6H_5CH_2^\bullet + t\text{-}BuOH \text{ and } C_6D_5CD_3 + t\text{-}BuO^\bullet \xrightarrow{k_D} C_6D_5CD_2^\bullet + t\text{-}BuOD$$

Since benzylic C–H is rather stronger[19] than the previous O–H and S–H, *tert*-butoxy radical could then undergo somewhat comparable abstraction and fragmentation with

---

(16) The direct competition[2] involves measurement of the ratio of the rate constants, k_Y/k_H, obtained from the relative rates of disappearence of YC_6H_4SH and C_6H_5SH.

(17) The indirect competition[2] uses fragmentation of *tert*-butoxy radical as a reference reaction to express the relative reactivities as k_Y/k_d.

(18) *Reaction Rates of Isotopic Molecules*; Melander, L., Saunders, W. H., Jr., Eds.; Wiley: New York, 1980.

(19) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

Table III. Primary Deuterium Kinetic Isotope Effects in the Hydrogen Abstractions at 130 °C

$$C_6H_5X\text{–}H(D) + t\text{-}BuO^{\bullet} \xrightarrow{k_{H(D)}} C_6H_5X^{\bullet} + t\text{-}BuOH(D),\ X = S \text{ and } O$$

$$C_6H_5CH_2\text{–}H(C_6D_5CD_2\text{–}D) + t\text{-}BuO^{\bullet} \xrightarrow{k_{H(D)}} C_6H_5CH_2^{\bullet}\ (C_6D_5CD_2^{\bullet}) + t\text{-}BuOH(D)$$

isotopic substrates C_6H_5X–H vs C_6H_5X–D	k_H/k_D[a,b]		
	CCl_4	C_6H_6	CH_3CN
(C_6H_5O–H vs C_6H_5O–D)[c]	1.33 ± 0.02	1.40 ± 0.19	2.79 ± 0.03
(C_6H_5S–H vs C_6H_5S–D)[c]	1.02 ± 0.04	1.05 ± 0.05	1.07 ± 0.03
($C_6H_5CH_3$ vs $C_6D_5CD_3$)[d]	6.76 ± 0.06	4.40 ± 0.20	5.38 ± 0.20

[a] Average values of more than three runs. [b] The theoretical maximum value of k_H/k_D is 6.88 at 27 °C, which becomes k_H/k_D = 4.20 at 130 °C, our reaction temperature. [c] Obtained by direct competitions.[2,16] [d] The rates were obtained by indirect competition[2,17] and cannot represent the conventional PDKIE because of the deuterations with $C_6D_5CD_3$.

the latter serving as the reference, which allowed measurements of the relative rates of the abstractions as k_H/k_d and k_D/k_d (indirect method).[2,17] The magnitudes of k_H/k_d and k_D/k_d could be calculated from

$$k_H/k_d = [t\text{-BuOH}]/[CH_3COCH_3]\cdot 1/[C_6H_5CH_3] \quad (8a)$$

and

$$k_D/k_d = [t\text{-BuOD}]/[CH_3COCH_3]\cdot 1/[C_6D_5CD_3] \quad (8b)$$

The k_H/k_D obtained here may not, however, represent conventional PDKIE due to deuterations of the phenyl ring of $C_6D_5CD_3$.

Structures of Polar TS Related with ρ^+ and k_H/k_D. The reactions of YC_6H_4SH show the best Hammett relations with σ^+ to exhibit rather constant $\rho^+ = -0.30$ for the several solvents (see Table I), which must tell the intervention of polar TS also taking place with other reactions.[10,20–24] The charge-transfer interaction between solvent and TS had been excluded[2] because transient TS dipole may not[6,25] survive the orientation of solvent dipole for the interaction. The solvation of *tert*-butoxy radical may therefore be solely responsible for alterations of rates of the abstractions.

tert-Butoxy radical abstracts hydrogen from C_6H_5SH ($t\text{-}BuO^{\bullet} + C_6H_5S\text{–}H \rightarrow t\text{-}BuOH + C_6H_5S^{\bullet}$) with $\Delta H = -22$ kcal/mol[19] and $E_a \ll 3$ kcal/mol.[26] The large exothermicity with relatively small activation energy could correspond to reactant-like TS: $[C_6H_5S{\cdot\cdot}H{\cdot\cdot\cdot\cdot}OC(CH_3)_3]^{\ddagger}$ according to the Hammond postulate.[27] Since the TS may experience very little H····O bond formation, the free energies of activation could be relatively immune to reactivities of solvated *tert*-butoxy radicals, which could give almost invariable values of k_Y/k_H listed in Table I. The unsymmetrical[18] TS structures are also consistent with modest PDKIE, i.e. k_H/k_D = 1.02–1.07 in CCl_4, C_6H_6, and CH_3CN (refer to Table III). The $\rho^+ = -0.30$ here appears comparable to $\rho^+ = -0.42$ for hydrogen abstractions from toluenes in C_6H_6 at 130 °C.[22] The sulfur atom of YC_6H_4SH could be subject to far more polarizability[28] than the benzylic carbon atom of $YC_6H_4CH_3$. The studies of PDKIE for reactions of toluenes (k_H/k_D = 4.17 and 5.40)[29,30] indicated that the TS may involve substantial benzylic C···H breaking. The comparable ρ^+ values should thus be derived from different origins, the former ($\rho^+ = -0.30$) from polarizability[28] and the latter ($\rho^+ = -0.42$) from degree of bond breaking.[31] *tert*-Butoxy radical[7] showed no tendency of electron transfer with *p*-dimethoxybenzene, which can exclude a similar role for YC_6H_5SH because C_6H_5SH appears more reactive than C_6H_5OH with the rate constants $k = 10^8\text{–}10^9\ M^{-1}\ s^{-1}$ at 22 °C toward *tert*-butoxy radical for hydrogen abstraction.

Profound solvent interactions are disclosed for the hydrogen abstractions from YC_6H_4OH (refer to Table II). The trend of ρ^+, i.e. $\rho^+ = -1.81$ (CCl_4), −1.46 (C_6H_6), and −1.02 (CH_3CN), parallels that of previous work,[10] with $\rho^+ = -1.19$ (CCl_4) and −0.79 (C_6H_5Cl), both at 122 °C. Since the free energy of solvation of *tert*-butoxy radical follows the sequence[2] $CH_3CN > C_6H_6 > CCl_4$, the H-bonding between *tert*-butoxy radical and phenolic O–H should be most effective in CCl_4 to accelerate significant H··O making subsequently followed by correspondingly greater O····H breaking with formation of product-like TS: $[YC_6H_4O{\cdot\cdot\cdot\cdot}H{\cdot\cdot}OC(CH_3)_3]^{\ddagger}$. The unsymmetrical TS structure in CCl_4 agrees very well with large[31] $\rho^+ = -1.81$ and small[18] k_H/k_D = 1.33 (refer to Table III). CH_3CN could provide stronger solvation than CCl_4, and tend accordingly to render the H-bonding less effective, which may eventually lead to less vigorous making and breaking of the bonds for the TS. The smaller $\rho^+ = -1.02$ (CH_3CN) (refer to Table II) could be thus consistent with less[31] O····H cleavage. The weakening of H-bonding via the solvation of *tert*-butoxy radical, assists the TS to approach a more symmetrical structure, which has been moderately exemplified in changes of PDKIE, i.e. k_H/k_D = 1.33 (CCl_4), 1.40 (C_6H_6), and 2.79 (CH_3CN) (refer to Table III).

The solvent effects on benzylic hydrogen abstractions[20] manifested modest alterations of Hammett correlations which hardly admitted plausible interrelations with solvent polarities, that is $\rho^+ = -0.35$ (Freon 113), −0.32 (C_6H_5Cl), and −0.39 (CH_3CN). The reactions of toluenes

$$C_6H_5CH_3(D_3) + t\text{-}BuO^{\bullet} \xrightarrow{k_{H(D)}} C_6H_5CH_2(D_2)^{\bullet} + t\text{-}BuOH(D)$$

provided forthcoming information as follows: $k_H = 2.3 \times 10^5\ M^{-1}\ s^{-1}$ at 22 °C in C_6H_6,[32] k_H/k_D = 5.40 and 4.17 at 40 °C in Freon 113,[29] and C_6H_5Cl,[30] respectively, and E_a = 5.6 kcal/mol.[33] The data may signify that the TS $[C_6H_5CH_2{\cdot\cdot\cdot}H{\cdot\cdot\cdot}OC(CH_3)_3]^{\ddagger}$ undergoes significant bond rupture and formation with the former more developed with positive E_a = 5.6 kcal/mol. While the magnitude of ρ^+ has been taken as a measure of bond breaking,[31] the solvation of *tert*-butoxy radical appears to influence more directly H···O formation than C···H cleavage (vide supra). The ambiguous solvent effect[20] on ρ^+ should be the

---

(20) Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1967**, *89*, 458.

(21) Kim, S. S.; Sohn, S. C. *Tetrahedron Lett.* **1982**, *23*, 3703.

(22) Kim, S. S.; Koo, H. M.; Choi, S. Y. *Tetrahedron Lett.* **1985**, *26*, 891.

(23) Mahiou, B.; Gleicher, G. J. *J. Org. Chem.* **1987**, *52*, 1555.

(24) Jones, M. J.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Org. Chem.* **1989**, *54*, 1607.

(25) Kim, S. S.; Lee, C. S.; Kim, C. C.; Kim, H. J. *J. Phys. Org. Chem.* **1990**, *3*, 803.

(26) Estimated from Kerr, J. A. *Handbook of Biomolecular and Termolecular Gas Reactions*; CRC Press.: Boca Raton, Florida, 1981; Vol. I.

(27) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(28) Kim, S. S.; Seo, J. S.; Yoon, M. H. *J. Org. Chem.* **1987**, *52*, 3691.

(29) Lewis, E. S.; Ogino, K. *J. Am. Chem. Soc.* **1976**, *98*, 2264.

(30) Larson, G. F.; Gilliom, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 3444.

(31) Russell, G. A. *J. Org. Chem.* **1958**, *23*, 1407.

Table IV. Relative Reactivities of Various Unsubstituted Substrates ($C_6H_5X{-}H$) toward *tert*-Butoxy Radical and the Hammett Correlations for the Abstractions from Substituted Ones ($YC_6H_4X{-}H$) at 130 °C in C_6H_6

$$C_6H_5X{-}H + t\text{-}BuO^\bullet \xrightarrow{k_a} C_6H_5X^\bullet + t\text{-}BuOH;\ t\text{-}BuO^\bullet \xrightarrow{k_d} CH_3^\bullet + CH_3COCH_3$$

$C_6H_5X{-}H$	k_a/k_d	ρ^+	$C_6H_5X{-}H$	k_a/k_d	ρ^+
$C_6H_5CH_2{-}H$[a]	0.064	−0.42	$C_6H_5NH{-}H$[c]	50.5	−1.24
$C_6H_5CH{=}NC_6H_5$[a]	0.82	−0.98	$C_6H_5O{-}H$[d]	88	−0.78
$C_6H_5CH{=}O$[b]	13.3	−0.32	$C_6H_5S{-}H$[e]	>88	−0.30

[a] Reference 22. [b] Reference 21. [c] Unpublished results from this laboratory. [d] Reference 10, where the solvent is C_6H_5Cl and the temperature 122 °C. [e] From Table I.

consequence of such secondary interference between bond cleavage and solvation. The PDKIE for reaction of toluene were investigated by several workers[29,30] at the same temperature, 40 °C [Lewis et al.,[29] $k_H/k_D = 5.40$ (Freon 113); Gilliom et al.,[30] $k_H/k_D = 4.17$ (C_6H_5Cl)]. The decrement with $k_H/k_D = 4.17$ (C_6H_5Cl)[30] can be real and due to weaker H···O bond formation caused by stronger solvation of *tert*-butoxy radical with C_6H_5Cl. The symmetry[18] of TS may thus be controlled by free energies of the solvation of *tert*-butoxy radical, which could be further verified by variations of PDKIE with solvents as disclosed in the reactions of $C_6H_5CH_3/C_6D_5CD_3$, i.e. $k_H/k_D = 6.76$ (CCl_4), 4.40 (C_6H_6), and 5.38 (CH_3CN) (refer to Table III).

Hammett ρ^+ as a Selectivity Parameter and Breakdowns of Reactivity/Selectivity Principle. In the absence of solvent interactions, *tert*-butoxy radical[2] was about 11 times more selective than chlorine atom[3] at 40 °C in the abstractions of tertiary H and primary H from DMB, i.e. $k_t/k_p = 44$ and 3.9 for the former and latter, respectively. Since *tert*-butoxy radical carries less reactivity,[26] its higher selectivity may well entertain the classical RSP.[4] The hydrogen abstractions[6,7,10,20–25,28,35] from substrates having toluene-like structures[34] exhibited negative ρ^+ values, which can be taken as selectivity parameters. We point out peculiar phenomena involved with the abstractions which should call validity of RSP into question. *tert*-Butoxy radical[20] and chlorine atom[35] abstracted hydrogens from toluenes to give the Hammett correlations, respectively, as follows: $\rho^+ = -0.35$ (Freon 113) at 45 °C[20] and $\rho^+ = -0.66$ (CCl_4) at 40 °C.[35] Considering minor variations of the reaction conditions, the less reactive[26] *tert*-butoxy radical could be regarded as also less selective, which is the opposite to the trend of selectivities mentioned earlier for the case of DMB.[2,3] Remarkable solvent effects can be recognized from Table II and more strongly solvated *tert*-butoxy radicals tend to be again less selective, i.e. $\rho^+ = -1.81$ (CCl_4), −1.46 (C_6H_6), −1.02 (CH_3CN). The identical reactions[7] were discovered interestingly to exhibit the same non-RSP behavior against temperature change, where ρ^+ in $C_6H_5CH_3$ can be calculated from Table III in ref 7 to be $\rho^+ = -0.88$ (22 °C), −0.68 (0 °C), −0.62 (−30 °C), and −0.48 (−60 °C). Similar temperature effects[6] on ρ^+ were already attributed to entropy control of selectivity stemming from polar TS. The reactions of toluenes[20] and thiophenols (Table I) indicate ambiguous roles of solvent for ρ^+ although the solvations should evidently alleviate reactivity of *tert*-butoxy radical toward hydrogen abstractions. The validity of RSP can be further obscured with Table IV, where increase of k_a/k_d accompanies random variations of ρ^+.

When reactions follow the Hammond postulate,[27] they could behave according to RSP[4] so that free energies of activation ($\Delta G^{\ddagger}$) can be linearly related with free energies of reaction (ΔG°). Many heterolytic reactions however have damaged[5] the RSP, whose reactivities could be amenable to anti-Hammond effect,[11–13] giving rise to "imbalanced TS" originally introduced by Jencks.[36] The concept of "imbalanced TS" has been recently elaborated with the "principle of nonperfect synchronization" (PNS).[37] The PNS[37] maintains that substituent effects on TS (kinetic substituent effects) can differ from those on reactant and product (thermodynamic substituent effects). The dualism of substituent effects should accordingly disrupt linear relation between $\Delta G^{\ddagger}$ and ΔG° for the heterolyses.

The homolytic reactions involving $\rho^+ < 0$[6,7,10,14,20–25,28,35] should traverse polar TS, a sort of "imbalanced TS",[36] which could likewise[37] prohibit the linear relation for $\Delta G^{\ddagger}$ and ΔG°. The Marcus equation,[15] $\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \Delta G^{\circ}/2 + (\Delta G^{\circ})^2/(16\Delta G_0^{\ddagger})$, can also provide a means of verification for the aforementioned nonlinearity by adopting a notion of variable intrinsic barriers ($\Delta G_0^{\ddagger}$), entities solely related to TS. When radical reactions were to proceed via homolytic TS, their intrinsic barriers might be exposed to little substituent effects because $\sigma^{\bullet}$[38] changes very little with substituents. The situation could become entirely different for the polar TS, where σ^{+}[39] then renders intrinsic barriers to experience drastic fluctuations. The free energies of activation ($\Delta G^{\ddagger}$) could therefore be influenced not only by the free energies of reaction (ΔG°) but also by the intrinsic barriers ($\Delta G_0^{\ddagger}$) to prevent the linear relation with the violations of RSP.

While the Hammett correlations for the hydrogen abstractions by *tert*-butoxy radical gave variable $\rho^+ < 0$ depending upon the substrates,[7,10,20–22] the rates were still more seriously affected by substituents than solvents. The hydrogen abstractions from toluenes[20] and thiophenols (Table I) suggest quite modest solvent effects on the rates. Only reactions of phenols (Table II) may exhibit rather conspicuous solvent interactions plausibly due to the H-bonding mentioned earlier. The solvations of *tert*-butoxy radical with various media could involve diverse free energies of solvation. When the variously solvated *tert*-butoxy radcials then abstract hydrogen from a substrate, the activated complexes may involve varying

---

(32) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(33) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69.

(34) The bond undergoing cleavage is situated at the β-position to the phenyl ring in a toluene-like structure, where conjugations could take place with the homolyic rupture.

(35) Russell, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 2357.

(36) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(37) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9; *Adv. Phy. Org. Chem.* **1992**, *27*, 119.

(38) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221.

(39) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

degrees of bond makings and breakings to determine the various free energies of activation ($\Delta G^{\ddagger}$) (kinetic solvent effects). The previous studies on the solvent effects[2] proposed two different states of solvations of *tert*-butoxy radical (dual solvations), where only the weakly solvated one could be capable of the hydrogen abstractions. Such dual solvations of *tert*-butoxy radical may provide a basis for the dualism of solvent effects on $\Delta G^{\ddagger}$ (kinetic solvent effects) and ΔG° (thermodynamic solvent effects) to become one of the prime factors causing the non-RSP behavior.

A much broader spectrum of reactivities, i.e. k_a/k_d in Table IV, is observed with variations of molecular structures. Each series of related reactions shows the Hammett correlations with $\rho^+ < 0$ standing for polar TS. When the homolytic reactions proceed through polar TS, the substituent operates in a different manner to change ΔG° and $\Delta G^{\ddagger}$ (dual substituent effects). A sequence of reactivities arrayed according to the structures may not necessarily match the trend of ρ^+ determined under the influence of the dual substituent effects.

Conclusion

tert-Butoxy radical exhibits unique behavior of solvation (dual solvations) which can be distinguished from those of chlorine[3] and bromine[25] atom. The dualisms of substituent and solvent effects can be the characteristic phenomena for the kinetically controlled reactions enjoying entropic dominance. Either temperature[7] or solvent can induce breakdowns of RSP for the hydrogen abstractions by *tert*-butoxy radical.

Experimental Section

Materials. All the reagents were commercially available from a major supplier. Liquids were fractionally distilled, and solids were either recrystallized or sublimed according to standard procedures.[40] C_6H_5SH and C_6H_5OH were deuterated,[41] and NMR (Varian EM 360L) spectra show 98.0% and 99.2% deuteration, respectively.

Competition Reactions. The compositions of the reaction mixtures are shown below with titles of the reactions. They were dissolved in appropriate solvents and placed in sealed degassed Pyrex ampules by freeze–pump–thaw method. The ampules were then heated in an oil bath at 130 °C for ca. 3 h and quenched in ice water, which were followed by gas chromatographic analyses.

Competitive hydrogen abstractions from pairs of YC_6H_4SH/C_6H_5SH in CCl_4, C_6H_6, and CS_2 (2 M)/CCl_4: YC_6H_4SH (0.1 M), C_6H_5SH (0.1 M), C_6H_5Cl (internal standard (IS), 0.1 M), and *tert*-butyl peroxide (TBP, 0.05 M).

Competition between hydrogen abstractions from YC_6H_4SH and fragmentation of *tert*-butoxy radical in CH_3CO_2H: YC_6H_4SH (0.05, 0.1, and 0.15 M), C_6H_5Cl (IS, 0.1 M), and TBP (0.05 M).

Competitive hydrogen abstractions from pairs of YC_6H_4OH/C_6H_5OH in CCl_4, C_6H_6, and CH_3CN: YC_6H_4OH (0.1 M), C_6H_5OH (0.1 M), C_6H_5Br (IS, 0.1 M), and TBP (0.05 M).

Competitive hydrogen (deuterium) abstractions from pairs of C_6H_5SH/*p*-ClC_6H_4SH and C_6H_5SD/*p*-ClC_6H_4SH in CCl_4, C_6H_6, and CH_3CN: $C_6H_5SH(D)$ (0.1 M), *p*-ClC_6H_4SH (0.1 M), C_6H_5Cl (IS, 0.1 M), and TBP (0.05 M).

Competitive hydrogen (deuterium) abstractions from pairs of C_6H_5OH/*p*-BrC_6H_4OH and C_6H_5OD/*p*-BrC_6H_4OH in CCl_4, C_6H_6, and CH_3CN: $C_6H_5OH(D)$ (0.1 M), *p*-BrC_6H_4OH (0.1 M), C_6H_5Br (IS, 0.1 M), and TBP (0.05 M).

Competition between hydrogen (deuterium) abstractions from $C_6H_5CH_3$ ($C_6D_5CD_3$) and fragmentation of *tert*-butoxy radical in CCl_4, C_6H_6, and CH_3CN: $C_6H_5CH_3$ ($C_6D_5CD_3$) (0.2, 0.4, and 0.6 M), C_6H_5Cl (IS, 0.1 M), and TBP (0.05 M).

Analytical Procedures. Analyses were carried out by GLC using a Varian 4600 or Varian 3300 equipped with a flame ionization or thermal conductivity detector. The columns were of 6-ft lengths of $^1/_8$ in. tubing packed with 10% SE-30, 15% FFAP, or 15% DIDP on Chromosorb W, depending on the system to be analyzed. Phenols were analyzed on 30 m × 0.32 mm fused silica capillary columns with bonded phase DB-1701 or DB-WAX, which were purchased from J&W SCIENTIFIC. The chromatographic resolutions were optimum with temperature programming from 60 °C to 200 °C.

Acknowledgment. We warmly thank the Ministry of Education for the Basic Science Programme Fund granted to Seoul National University. Financial support from Korea Science and Engineering Foundation and Organic Chemistry Research Center is gratefully acknowledged. Generous support (1992) was also provided from Inha University.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; *t*-BuO, 3141-58-0; *p*-$MeOC_6H_4SH$, 696-63-9; *p*-MeC_6H_4SH, 106-45-6; *p*-FC_6H_4SH, 371-42-6; PhSH, 108-98-5; *p*-ClC_6H_4SH, 106-54-7; *p*-BrC_6H_4SH, 106-53-6; *p*-$MeOC_6H_4OH$, 150-76-5; *p*-MeC_6H_4OH, 106-44-5; PhOH, 108-95-2; *p*-ClC_6H_4OH, 106-48-9; MePh, 108-88-3; $PhNH_2$, 62-53-3.

---

[40] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: Oxford, 1980.

[41] Verbit, L. *Synthesis* 1972, 254.