

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

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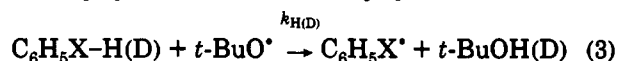
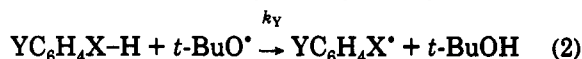
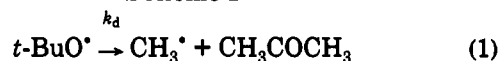
The Hammett correlations and primary deuterium kinetic isotope effects were obtained to investigate the solvent effects on hydrogen abstractions from thiophenols, phenols, and toluenes by *tert*-butoxy radical, where the latter proved to be a more sensitive probe than the former. The limitations of the 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 radical² 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 atom³ 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 radical² with $k_t/k_p = 44$ at 40 °C than for equivalent chlorine atom³ 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/selectivity 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 violate⁵ 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 $2.303 \log(A_t/A_p) = (\Delta S_t^\ddagger - \Delta S_p^\ddagger)/R$, 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 phenols¹⁰ to exhibit quite unidentical Hammett correlations with different solvents, that is $\rho^+ = -1.19$ (CCl₄) and $\rho^+ = -0.79$ (C₆H₅Cl), both at 122 °C. Since ρ^+ can be also taken as a selectivity parameter, the solvation with C₆H₅Cl renders *tert*-butoxy radical to carry less reactivity and selectivity than in the case of CCl₄, which again denies the well-known inverse relationship.⁴ The failures⁵ 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 carbinoyloxy radicals¹⁴ could be the first example of homolytic reactions defying the authority of RSP⁴ 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



X = O and S

Results and Discussion

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

(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 C₆H₅CH₃.

(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.

[†] Dedicated to professor Cheves Walling.

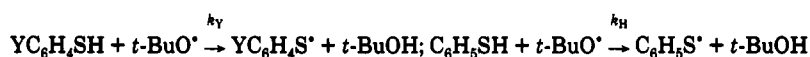
(1) Presented at the 3rd European Symposium on Organic Reactivity, Göteborg, Sweden, July 7-12, 1991.

(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.

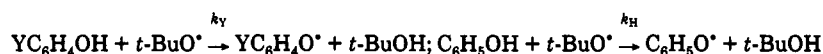
(4) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963.

(5) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (b) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755. (c) Pross, A. *Adv. Phys. 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) Buncl, E.; Wilson, H. *J. Chem. Educ.* **1987**, *64*, 476.

Table I. Relative Reactivities of YC₆H₄SH toward *tert*-Butoxy Radical and Hammett Correlations at 130 °C

solvents	$k_Y/k_H;^a Y =$						Hammett correlations	
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -F	H	<i>p</i> -Cl	<i>p</i> -Br	$\rho^{+b} (r)^c$	$\rho^b (r)^c$
CCl ₄ ^{d,e}	1.76	1.30	1.18	1	1.01	0.92	-0.30 (0.985)	-0.49 (0.889)
C ₆ H 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 ₃ CO ₂ H ^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. YC₆H₄SH = C₆H₅S[•] = YC₆H₄S[•] = C₆H₅SH, 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 YC₆H₄OH toward *tert*-Butoxy Radical and Hammett Correlation at 130 °C

solvent	$k_Y/k_H;^a,b Y =$				Hammett correlations	
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	H	<i>p</i> -Cl	$\rho^{+c} (r)^d$	$\rho^c (r)^d$
CCl ₄	29.65	6.24	1	0.85	-1.81 (0.990)	-3.01 (0.905)
C ₆ H ₆	13.98	3.62	1	0.73	-1.46 (0.996)	-2.46 (0.919)
CH ₃ CN	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. YC₆H₄OH = C₆H₅O[•] = YC₆H₄O[•] = C₆H₅OH, should be insignificant not to alter the rates. ^c Plotted against σ^+ for ρ^+ and σ for ρ . ^d Correlation coefficients.

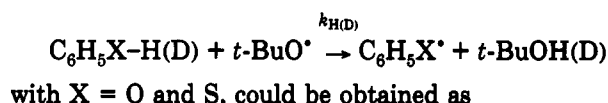
Effects. The relative rates of hydrogen abstractions from YC₆H₄SH by *tert*-butoxy radical in CCl₄, C₆H₆, and CS₂ (2 M)/CCl₄ were obtained with C₆H₅SH as a standard substrate using

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

where *Y* and *H* represent respectively molar concentrations of YC₆H₄SH and C₆H₅SH with subscripts *f* and *i* standing for final and initial, respectively (direct competition).^{2,16} The same reactivities in CH₃CO₂H could be derived from

$$k_Y/k_d = ([t\text{-BuOH}]/[\text{CH}_3\text{COCH}_3]) \cdot 1/[\text{YC}_6\text{H}_4\text{SH}] \quad (5)$$

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 CH₃CO₂H because H-bonding between *tert*-butoxy radical and CH₃CO₂H may slow down the rate of abstraction which appears otherwise⁷ 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 YC₆H₄OH in CCl₄, C₆H₆, and CH₃CN 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. C₆H₅OH/C₆H₅OD, C₆H₅SH/C₆H₅SD, and C₆H₅CH₃/C₆D₅CD₃ (Table III). The k_H/k_D for

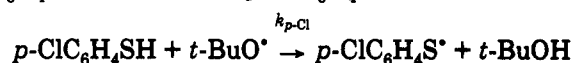
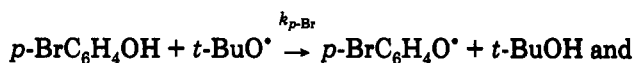


$$k_H/k_D = (k_H/k_{p\text{-Br}})(k_{p\text{-Br}}/k_D) \quad (6a)$$

when X = O and

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

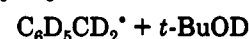
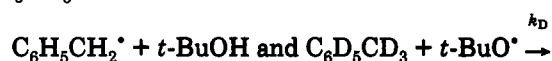
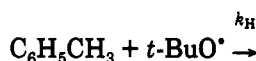
when X = S, where



The values of $k_H/k_{p\text{-Br}}$ and $k_D/k_{p\text{-Br}}$ were then available from direct competition method¹⁶ with pairs of C₆H₅OH/*p*-BrC₆H₄OH and C₆H₅OD/*p*-BrC₆H₄OH, respectively. Similar procedures provided figures for $k_H/k_{p\text{-Cl}}$ and $k_D/k_{p\text{-Cl}}$ from the competitions of C₆H₅SH/*p*-ClC₆H₄SH and C₆H₅SD/*p*-ClC₆H₄SH, respectively. The PDKIE were calculated from

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

for



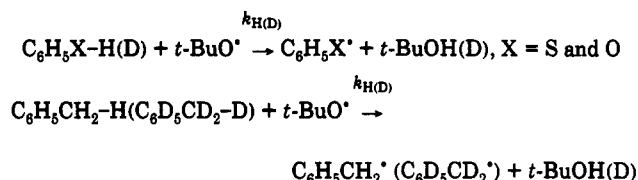
Since benzylic C-H is rather stronger¹⁹ than the previous O-H and S-H, *tert*-butoxy radical could then undergo somewhat comparable abstraction and fragmentation with

(16) The direct competition² involves measurement of the ratio of the rate constants, k_Y/k_H , obtained from the relative rates of disappearance of YC₆H₄SH and C₆H₅SH.

(17) The indirect competition² 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

isotopic substrates C ₆ H ₅ X-H vs C ₆ H ₅ X-D	k _H /k _D ^{a,b}		
	CCl ₄	C ₆ H ₆	CH ₃ CN
(C ₆ H ₅ O-H vs C ₆ H ₅ O-D) ^c	1.33 ± 0.02	1.40 ± 0.19	2.79 ± 0.03
(C ₆ H ₅ S-H vs C ₆ H ₅ S-D) ^c	1.02 ± 0.04	1.05 ± 0.05	1.07 ± 0.03
(C ₆ H ₅ CH ₃ vs C ₆ D ₅ CD 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 C₆D₅CD₃.

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

$$k_{\text{H}}/k_{\text{d}} = [t\text{-BuOH}]/[\text{CH}_3\text{COCH}_3] \cdot 1/[\text{C}_6\text{H}_5\text{CH}_3] \quad (8a)$$

and

$$k_{\text{D}}/k_{\text{d}} = [t\text{-BuOD}]/[\text{CH}_3\text{COCH}_3] \cdot 1/[\text{C}_6\text{D}_5\text{CD}_3] \quad (8b)$$

The k_H/k_D obtained here may not, however, represent conventional PDKIE due to deuterations of the phenyl ring of C₆D₅CD₃.

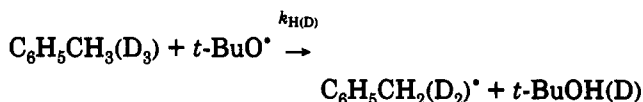
Structures of Polar TS Related with ρ⁺ and k_H/k_D. The reactions of YC₆H₄SH show the best Hammett relations with σ⁺ to exhibit rather constant ρ⁺ = -0.30 for the several solvents (see Table I), which must tell the intervention of polar TS also taking place with other reactions.^{10,20-24} The charge-transfer interaction between solvent and TS had been excluded² 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 C₆H₅SH (t-BuO[•] + C₆H₅S-H → t-BuOH + C₆H₅S[•]) with ΔH = -22 kcal/mol¹⁹ and E_a << 3 kcal/mol.²⁶ The large exothermicity with relatively small activation energy could correspond to reactant-like TS: [C₆H₅S-H...OC(CH₃)₃][•] 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 unsymmetrical¹⁸ TS structures are also consistent with modest

PDKIE, i.e. k_H/k_D = 1.02-1.07 in CCl₄, C₆H₆, and CH₃CN (refer to Table III). The ρ⁺ = -0.30 here appears comparable to ρ⁺ = -0.42 for hydrogen abstractions from toluenes in C₆H₆ at 130 °C.²² The sulfur atom of YC₆H₄SH could be subject to far more polarizability²⁸ than the benzylic carbon atom of YC₆H₄CH₃. 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 (ρ⁺ = -0.30) from polarizability²⁸ and the latter (ρ⁺ = -0.42) from degree of bond breaking.³¹ *tert*-Butoxy radical⁷ showed no tendency of electron transfer with *p*-dimethoxybenzene, which can exclude a similar role for YC₆H₅SH because C₆H₅SH appears more reactive than C₆H₅OH with the rate constants k = 10⁸-10⁹ M⁻¹ s⁻¹ at 22 °C toward *tert*-butoxy radical for hydrogen abstraction.

Profound solvent interactions are disclosed for the hydrogen abstractions from YC₆H₄OH (refer to Table II). The trend of ρ⁺, i.e. ρ⁺ = -1.81 (CCl₄), -1.46 (C₆H₆), and -1.02 (CH₃CN), parallels that of previous work,¹⁰ with ρ⁺ = -1.19 (CCl₄) and -0.79 (C₆H₅Cl), both at 122 °C. Since the free energy of solvation of *tert*-butoxy radical follows the sequence² CH₃CN > C₆H₆ > CCl₄, the H-bonding between *tert*-butoxy radical and phenolic O-H should be most effective in CCl₄ to accelerate significant H...O making subsequently followed by correspondingly greater O...H breaking with formation of product-like TS: [YC₆H₄O...H...OC(CH₃)₃][•]. The unsymmetrical TS structure in CCl₄ agrees very well with large³¹ ρ⁺ = -1.81 and small¹⁸ k_H/k_D = 1.33 (refer to Table III). CH₃CN could provide stronger solvation than CCl₄, 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 ρ⁺ = -1.02 (CH₃CN) (refer to Table II) could be thus consistent with less³¹ 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 (CCl₄), 1.40 (C₆H₆), and 2.79 (CH₃CN) (refer to Table III).

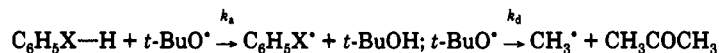
The solvent effects on benzylic hydrogen abstractions²⁰ manifested modest alterations of Hammett correlations which hardly admitted plausible interrelations with solvent polarities, that is ρ⁺ = -0.35 (Freon 113), -0.32 (C₆H₅Cl), and -0.39 (CH₃CN). The reactions of toluenes



provided forthcoming information as follows: k_H = 2.3 × 10⁵ M⁻¹ s⁻¹ at 22 °C in C₆H₆,³² k_H/k_D = 5.40 and 4.17 at 40 °C in Freon 113,²⁹ and C₆H₅Cl,³⁰ respectively, and E_a = 5.6 kcal/mol.³³ The data may signify that the TS [C₆H₅CH₂...H...OC(CH₃)₃][•] 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 effect²⁰ 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 (C₆H₅X-H) toward *tert*-Butoxy Radical and the Hammett Correlations for the Abstractions from Substituted Ones (YC₆H₄X-H) at 130 °C in C₆H₆

C ₆ H ₅ X-H	k_a/k_d	ρ^+	C ₆ H ₅ X-H	k_a/k_d	ρ^+
C ₆ H ₅ CH ₂ -H ^a	0.064	-0.42	C ₆ H ₅ NH-H ^c	50.5	-1.24
C ₆ H ₅ CH=NC ₆ H ₅ ^a	0.82	-0.98	C ₆ H ₅ O-H ^d	88	-0.78
C ₆ H ₅ CH=O ^b	13.3	-0.32	C ₆ H ₅ S-H ^e	>88	-0.30

^a Reference 22. ^b Reference 21. ^c Unpublished results from this laboratory. ^d Reference 10, where the solvent is C₆H₅Cl 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 $k_H/k_D = 4.17$ (C₆H₅Cl)]. The decrement with $k_H/k_D = 4.17$ (C₆H₅Cl)³⁰ can be real and due to weaker H...O bond formation caused by stronger solvation of *tert*-butoxy radical with C₆H₅Cl. The symmetry¹⁸ 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 C₆H₅CH₃/C₆D₅CD₃, i.e. $k_H/k_D = 6.76$ (CCl₄), 4.40 (C₆H₆), and 5.38 (CH₃CN) (refer to Table III).

Hammett ρ^+ as a Selectivity Parameter and Breakdowns of Reactivity/Selectivity Principle. In the absence of solvent interactions, *tert*-butoxy radical² was about 11 times more selective than chlorine atom³ 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 structures³⁴ 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 radical²⁰ and chlorine atom³⁵ abstracted hydrogens from toluenes to give the Hammett correlations, respectively, as follows: $\rho^+ = -0.35$ (Freon 113) at 45 °C²⁰ and $\rho^+ = -0.66$ (CCl₄) at 40 °C.³⁵ Considering minor variations of the reaction conditions, the less reactive²⁶ *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. $\rho^+ = -1.81$ (CCl₄), -1.46 (C₆H₆), -1.02 (CH₃CN). The identical reactions⁷ were discovered interestingly to exhibit the same non-RSP behavior against temperature change, where ρ^+ in C₆H₅CH₃ 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 effects⁶ on ρ^+ were already attributed to entropy control of selectivity stemming from polar TS. The reactions of toluenes²⁰ 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 RSP⁴ so that free energies of activation (ΔG^\ddagger) can be linearly related with free energies of reaction (ΔG°). Many heterolytic reactions however have damaged⁵ 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 PNS³⁷ 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 ΔG^\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 likewise³⁷ prohibit the linear relation for ΔG^\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 (ΔG_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 σ 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 (ΔG^\ddagger) could therefore be influenced not only by the free energies of reaction (ΔG°) but also by the intrinsic barriers (ΔG_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 toluenes²⁰ 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 radicals then abstract hydrogen from a substrate, the activated complexes may involve varying

(32) Paul, H.; Small, R. D., Jr.; Sciano, 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 homolytic 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. Phys. 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 (ΔG^\ddagger) (kinetic solvent effects). The previous studies on the solvent effects² 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 ΔG^\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 ΔG^\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 chlorine³ and bromine²⁵ atom. The dualisms of substituent and solvent effects can be the characteristic phenomena for the kinetically controlled reactions enjoying entropic dominance. Either temperature⁷ 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

(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.

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): 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 $C_6H_5SH/p\text{-}ClC_6H_4SH$ and $C_6H_5SD/p\text{-}ClC_6H_4SH$ in CCl_4 , C_6H_6 , and CH_3CN : $C_6H_5SH(D)$ (0.1 M), $p\text{-}ClC_6H_4SH$ (0.1 M), C_6H_5Cl (IS, 0.1 M), and TBP (0.05 M).

Competitive hydrogen (deuterium) abstractions from pairs of $C_6H_5OH/p\text{-}BrC_6H_4OH$ and $C_6H_5OD/p\text{-}BrC_6H_4OH$ in CCl_4 , C_6H_6 , and CH_3CN : $C_6H_5OH(D)$ (0.1 M), $p\text{-}BrC_6H_4OH$ (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 \times 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.

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Registry No. H_2 , 1333-74-0; D_2 , 7782-39-0; *t*-BuO, 3141-58-0; *p*-MeOC₆H₄SH, 696-63-9; *p*-MeC₆H₄SH, 106-45-6; *p*-FC₆H₄SH, 371-42-6; PhSH, 108-98-5; *p*-ClC₆H₄SH, 106-54-7; *p*-BrC₆H₄SH, 106-53-6; *p*-MeOC₆H₄OH, 150-76-5; *p*-MeC₆H₄OH, 106-44-5; PhOH, 108-95-2; *p*-ClC₆H₄OH, 106-48-9; MePh, 108-88-3; PhNH₂, 62-53-3.