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Homolytic Fragmentations of Benzyl Methyl Substituted-Benzyl Carbinyloxy Radicals and the Related Reactions: Limitations of the Leffler–Hammond Postulate and Reactivity/Selectivity Principle

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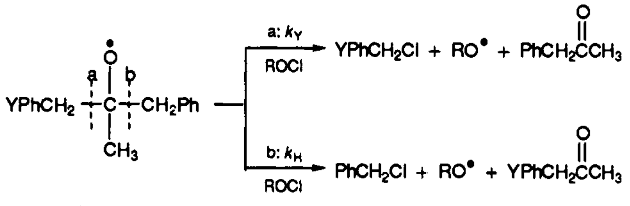
Abstract: Photolyses of benzyl methyl substituted-benzyl carbinyl hypochlorites produced the corresponding carbinyloxy radicals, which undergo fragmentations. Oxidations of 1-aryl-2,3-diphenylpropan-2-ols by ceric ammonium nitrate also proceeded through quite similar homolytic β-scissions. The relative rates and Hammett ρ^+ values are independent of temperatures. The differential activation parameters indicate that the entropic factors are important for the reactions. The differential entropic term ($\Delta S^{\ddagger}_{Y-H}$) could be related to the difference in the extent of bond cleavages caused by the different σ^+ values of the substituents, Y and H, in the polar transition state (TS). The selectivities (relative rates) remain constant or even increase with increasing temperature, indicating that the reactivities are controlled by entropy. The polar TS can be caused by the perpendicular effect to invite the dual substituent effects with breakdowns of the Leffler–Hammond postulate. The solvent effects on the reactions of the three oxygen radicals are compared. A new scheme is proposed for hydrogen abstractions by solvated *tert*-butoxy and cumyloxy radicals.

Introduction

Absolute rate theory[1] collaborates with the Bell–Evans–Polanyi principle[2,3] to yield the Leffler–Hammond postulate (LHP)[4,5] and reactivity/selectivity principle (RSP),[6] where the transition state (TS) is assumed to be the resonance hybrid of the reactant and the product. When the TS assumes such an intermediate configuration, the substituent effects on the free energy of activation ($\Delta G^{\ddagger}_{Y}$) (kinetic substituent effect) and free energy of reaction (ΔG°_{Y}) (thermodynamic substituent effect) are linearly related with each other. The parallelism between the rate and the equilibrium could be eminently accommodated with the two-dimensional reaction profile, whereby the LHP[4,5] and RSP[6] successfully predict numerous reactivities. The failures[7] were, however, recognized with many heterolytic reactions. Therefore the perpendicular effect[8] has been proposed and subsequently accommodated in the three-dimensional potential energy surface diagram (PESD).[9–11] The outcome of the perpendicular effect[8] could be alternatively understood in terms of Marcus theory[11,12] when the intrinsic barrier is drastically varied by the substituents (Y).[21] The multidimensional reaction profile[9–11] is further elaborated by the notion of an "imbalanced TS"[13] and the "principle of nonperfect synchronization (PNS)".[14] The evolutions of those concepts of chemical reactivity have been excellently reviewed recently.[15]

Scheme 1



ROCl: benzyl methyl substituted-benzyl carbinyl hypochlorite

YPh: YC_6H_4 Ph: C_6H_5

When the homolytic cleavages occur at the position β to the phenyl ring, i.e. $YPhCH_3 + X^{\bullet} \rightarrow YPhCH_2^{\bullet} + HX$, the reactions always traverse the polar TS, obeying excellent ρ^+–σ^+ correlations.[16–21] In some cases, temperature studies[19,20] betrayed entropic factors for the rates, where the selectivities (the relative rates) increased[19] or remained constant[20] with higher temperature, thus invalidating the RSP.[21] We now wish to report the reactivities of fragmentations of the carbinyloxy radicals[20] and the analogous reactions[22] where the polar TS could not be properly located on the two-dimensional reaction profile. The solvent interactions for the oxygen radicals[21,23,24] will subsequently be discussed.

Results

Photolyses of 0.07 M solutions of benzyl methyl substituted-benzyl carbinyl hypochlorites by sunlamp at several temperatures produced the corresponding carbinyloxy radicals, which then decomposed to benzyl radicals and ketones. Benzyl radicals were trapped by the hypochlorites to form benzyl chlorides (Scheme 1). The benzyl chlorides were analyzed by GLC and the relative rates (k_Y/k_H) calculated with

$$k_Y/k_H = [YPhCH_2Cl]/[PhCH_2Cl] \qquad (1)$$

The yields of the benzyl chlorides were essentially the same as those of the corresponding ketones, supporting the validity of eq 1.

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Table 1. Relative Rates and Hammett Correlations for β-Cleavages of Benzyl Methyl Substituted-Benzyl Carbinyloxy Radicals in CCl_4

	k_Y/k_H[a,b]						Hammett correlations	
temp (°C)	p-OCH_3[c]	p-CH_3	p-F	H	p-Cl	m-Cl	ρ^{+} [d] (r)[e]	ρ[d] (r)[e]
−20	4.91	1.73	1.07	1	(0.72)[f]	0.42	−0.90 (0.999)	−1.50 (0.946)
−10	4.78	1.64	1.07	1	(0.72)[f]	0.42	−0.89 (0.999)	−1.47 (0.942)
10	4.80	1.63	1.06	1	0.72	0.41	−0.90 (0.998)	−1.42 (0.913)
25	4.74	1.62	1.06	1	0.72	0.41	−0.89 (0.998)	−1.42 (0.943)
40	4.79	1.62	1.07	1	0.73	0.41	−0.89 (0.998)	−1.42 (0.941)
60	4.81	1.63	1.07	1	0.72	0.42	−0.89 (0.998)	−1.42 (0.941)

[a] Error limits are less than 3% with average deviations of more than three runs. [b] Substituent constants were taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 334. [c] $CaCO_3$ was added to the reaction mixture to stabilize p-$OCH_3C_6H_4Cl$ derived from reactions of the corresponding hypochlorite. [d] Plotted against σ^{+} for ρ^{+} and σ for ρ. [e] Correlation coefficient. [f] Taken from the value at 10 °C.

Table 2. Differential Activation Parameters for β-Cleavages of the Carbinyloxy Radicals in CCl_4

differentials	p-OCH_3	p-CH_3	p-F	H	p-Cl	m-Cl
$\Delta\Delta H^{\ddagger}_{Y-H}$[a]	−0.032	−0.100	−0.002	0	0.012	−0.025
$\Delta\Delta S^{\ddagger}_{Y-H}$[b]	3.01	0.640	0.123	0	−0.608	−1.83

[a] $\Delta\Delta H^{\ddagger}_{Y-H} = \Delta H^{\ddagger}_{Y} - \Delta H^{\ddagger}_{H}$, where $\Delta H^{\ddagger}_{Y}$ and $\Delta H^{\ddagger}_{H}$ are the activation enthalpies for the cleavages of substituted and simple benzyl radicals, respectively (unit: kcal/mol). [b] $\Delta\Delta S^{\ddagger}_{Y-H} = \Delta S^{\ddagger}_{Y} - \Delta S^{\ddagger}_{H}$, where $\Delta S^{\ddagger}_{Y}$ and $\Delta S^{\ddagger}_{H}$ are similarly related as in the above enthalpic terms (unit: eu).

Table 1 contains relative rates (k_Y/k_H) and Hammett constants (ρ^{+} and ρ) at various temperatures in CCl_4. Expansion of the temperature range from previous work[20] persistently reveals little variation of the relative rates. Differential activation parameters were derived using the Eyring equation[1] (Table 2), where the large values of entropic terms signify the importance of entropy for the rates. The solvent effect on the relative rates was investigated. The results are summarized in Table 3.

Oxidations of 1-aryl-2,3-diphenylpropan-2-ols with ceric ammonium nitrate (CAN)[22] were carried out in 85% aqueous acetic acid at temperatures from 20 to 120 °C. The alcohols initially undergo complexations with cerium(IV) ion, leading to electron transfer, which is followed by the homolytic cleavages (Scheme 2).

The benzyl radicals so produced are amenable to further oxidation by cerium(IV) ion while the ketones remain unaltered. The ratios of the two ketones represent the relative rate with

$$k_Y/k_H = [PhCH_2COPh]/[YPhCH_2COPh] \quad (2)$$

The rates (k_Y/k_H) and Hammett ρ^{+} values listed in Table 4 further demonstrate the absence of a temperature effect. The value of $\rho^{+} = -2.20$ is in good agreement with the previous value of $\rho^{+} = -1.91$.[22] Differential activation parameters are summarized in Table 5.

Entropic Contribution Responsible for Non-RSP Behavior. One can envision the following changes which control the entropy of the system during the β-scissions (Schemes 1 and 2). Vibration of the C–C bond should be replaced by a translational mode[1] to increase the entropy. On the other hand, the disappearance of the rotation of the bond and the hindered rotation derived from conjugation of the benzylic carbocationic center with the phenyl ring are expected to decrease it. Since translation implicates three dimensions while rotation and vibration are of two and one dimensions, respectively, the translational entropy enjoyed by the TS could far exceed the decrease of vibrational and rotational entropies. The excellent linear relations between $\Delta\Delta S^{\ddagger}_{Y-H}$ and σ^{+} (Figures 1 and 2) could be indications of such a contribution of translational entropy to the rates. A similar relationship between $\Delta\Delta S^{\ddagger}_{Y-H}$ and σ^{+} has been observed in the brominations of toluenes (refer to Figure 2 of ref 19).

The electron-donating substituents (Y) stabilize the benzylic carbocation moiety of the polar TS to increase the extent of the C–C bond breaking. The cleavages require the enthalpies of activation ($\Delta H^{\ddagger}_{Y}$) to be positive and provide the TS with remarkable translational degrees of freedom to boost the entropies of activation ($\Delta S^{\ddagger}_{Y}$) (a corollary of the isokinetic relation).[25] The degree of the bond breakages could be therefore a function of the σ^{+} of the substituents (Y), where the differential entropic terms ($\Delta\Delta S^{\ddagger}_{Y-H}$) (Tables 2 and 5) tend to decrease as the substituents (Y) become gradually electron withdrawing to give the negative slopes for Figures 1 and 2. The oxidative cleavages of 1-aryl-2,3-diphenylpropan-2-ols (Table 3) show the larger negative value of $\rho^{+} = -2.20$ compared to that of the fragmentations of carbinyloxy radicals ($\rho^{+} = -0.90$) (Table 1). The bigger magnitude of ρ^{+} could correspond to the more bond ruptures[18] involved in the polar TS of Scheme 2, which could be translated into the steeper slope of Figure 2 than that of Figure 1.

The selectivity S of a species in its reaction with the competing reagents harboring substituents Y and H could be defined by $S = \ln k_Y/k_H = -(\Delta G^{\ddagger}_{Y} - \Delta G^{\ddagger}_{H})/RT = -\Delta\Delta G^{\ddagger}_{Y-H}/RT$, with k and $\Delta G^{\ddagger}$ being the corresponding rate constant and free energy of activation, respectively. $S = -\Delta\Delta G^{\ddagger}_{Y-H}/RT$ can be subdivided into two parts: $-\Delta\Delta G^{\ddagger}_{Y-H}/RT = \Delta\Delta S^{\ddagger}_{Y-H}/R - \Delta\Delta H^{\ddagger}_{Y-H}/RT$.

The present homolytic reactions involve $\Delta\Delta H^{\ddagger}_{Y-H}/RT$ close to zero (Tables 2 and 5) with S mainly controlled by $\Delta\Delta S^{\ddagger}_{Y-H}/R$, which is temperature-independent (Tables 1 and 4). When the values of $\Delta\Delta H^{\ddagger}_{Y-H}$ are relatively small but not zero (Table 2 of ref 19), increase of temperature tends to reduce the magnitude of $\Delta\Delta H^{\ddagger}_{Y-H}/RT$, which should be subtracted[26] from $\Delta\Delta S^{\ddagger}_{Y-H}/R$ to determine S. This is tantamount to stating that increase of temperature boosts selectivities to higher values, a phenomenon apparently violating the RSP (refer to Table 1 of ref 19). The same line of reasoning for $S = -\Delta\Delta G^{\ddagger}_{Y-H}/RT = \Delta\Delta S^{\ddagger}_{Y-H}/R - \Delta\Delta H^{\ddagger}_{Y-H}/RT$ requires that S must decrease with increasing temperature when $\Delta\Delta H^{\ddagger}_{Y-H} \gg \Delta\Delta S^{\ddagger}_{Y-H}$, the manifestation of the RSP.

Dual Substituents Effect Incompatible with Leffler–Hammond Postulate. The ionizations of the cumyl chlorides[27] traverse a

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Table 3. Relative Rates and Hammett Correlations for β-Cleavages of the Carbinyloxy Radicals at 40 °C

	k_Y/k_H[a,b]						Hammett correlations	
solvent	p-OCH$_3$[c]	p-CH$_3$	p-F	H	p-Cl	m-Cl	ρ^+ [d] (r)[e]	ρ[d] (r)[e]
CCl$_4$	4.79	1.63	1.07	1	(0.72)[f]	0.41	–0.89 (0.998)	–1.42 (0.940)
cyclo-C_6H_{10}	4.85	1.77	0.98	1	(0.72)[f]	0.48	–0.86 (0.995)	–1.42 (0.936)
C_6H_6	4.75	1.62	1.06	1	0.72	0.41	–0.89 (0.998)	–1.42 (0.943)
CH_3CN	4.62	1.59	0.90	1	0.76	(0.41)[f]	–0.89 (0.990)	–1.42 (0.835)
$(CH_3)_3COH$	4.69	1.63	0.91	1	0.72	(0.41)[f]	–0.91 (0.993)	–1.46 (0.855)

[a] Error limits are within 3% with average deviations of more than three runs. [b] Substituent constants were taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 334. [c] $CaCO_3$ was added to the reaction mixture as the stabilizer for the reactions. [d] Plotted against σ^+ for ρ^+ and σ for ρ. [e] Correlation coefficient. [f] Taken from the value of C_6H_6.

Scheme 2

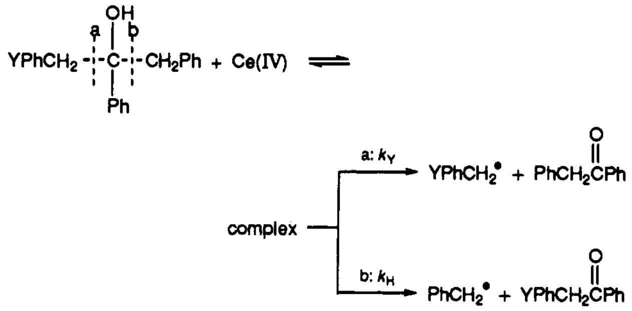

Table 4. Relative Rates and Hammett Correlations for Oxidation of 1-Aryl-2,3-diphenylpropan-2-ols by Cerium(IV) in 85% Aqueous Acetic Acid

	k_Y/k_H[a,b]				Hammett correlations	
temp (°C)	p-CH$_3$	p-F	H	p-Cl	ρ^+ [c] (r)[d]	ρ[e] (r)[d]
20	(5.05)[e]	1.26	1	0.627	–2.18 (0.995)	–2.18 (0.923)
60	5.05	1.22	1	0.628	–2.17 (0.993)	–2.18 (0.924)
85	5.41	1.32	1	0.646	–2.23 (0.995)	–2.21 (0.915)
120	5.09	1.31	1	0.606	–2.18 (0.993)	–2.23 (0.928)

[a] Error limits are ca. 5% with average deviations of more than three runs. Compared to GLC method (Tables 1 and 3), analyses by NMR showed less accuracy. [b] Substituent constants were taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 334. [c] Plotted against σ^+ for ρ^+ and σ for ρ. [d] Correlation coefficient. [e] Taken from the value at 60 °C.

Table 5. Differential Activation Parameters for Oxidation of 1-Aryl-2,3-diphenylpropan-2-ols by Cerium(IV) in 85% Aqueous Acetic Acid

differentials	p-CH$_3$	p-F	H	p-Cl
$\Delta\Delta H^\ddagger_{Y\text{-}H}$[a]	0.064	0.118	0	–0.045
$\Delta\Delta S^\ddagger_{Y\text{-}H}$[b]	3.44	0.834	0	–1.06

[a] $\Delta\Delta H^\ddagger_{Y\text{-}H} = \Delta H^\ddagger_Y - \Delta H^\ddagger_H$, where $\Delta H^\ddagger_Y$ and $\Delta H^\ddagger_H$ are the activation enthalpies for the cleavages of substituted and simple benzyl radicals, respectively (unit: kcal/mol). [b] $\Delta\Delta S^\ddagger_{Y\text{-}H} = \Delta S^\ddagger_Y - \Delta S^\ddagger_H$, where $\Delta S^\ddagger_Y$ and $\Delta S_H^\ddagger$ are similarly related as in the above enthalpic terms (unit: eu).

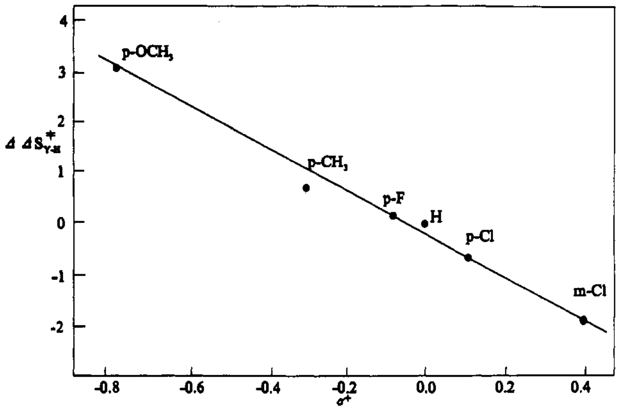

Figure 1. Plot of $\Delta\Delta S^\ddagger_{Y\text{-}H}$ vs σ^+ for the β-scissions.

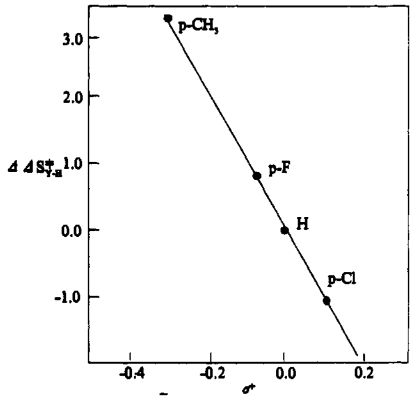

Figure 2. Plot of $\Delta\Delta S^\ddagger_{Y\text{-}H}$ vs σ^+ for the oxidative β-cleavages.

polar TS ($\rho^+ = -4.45$), which is equivalent to the resonance hybrid of the reactant and the product. The enthalpy of activation is thereby linearly related to the heat of formation of the cumyl carbocation. The former constitutes a major portion of the free energy of activation ($\Delta G^\ddagger_Y$) while the latter heavily contributes to the free energy of reaction (ΔG°_Y) to give parallelism between kinetic and thermodynamic substituent effects: $\Delta\Delta G^\ddagger_{Y\text{-}H} = \alpha\Delta\Delta G^\circ_{Y\text{-}H}$, where $0 < \alpha < 1$, $\Delta\Delta G^\ddagger_{Y\text{-}H} = \Delta G^\ddagger_Y - \Delta G^\ddagger_H$, and $\Delta\Delta G^\circ_{Y\text{-}H} = \Delta G^\circ_Y - \Delta G^\circ_H$, with the subscripts meaning the substituents on the phenyl ring.

The Hammett correlations of Tables 1 ($\rho^+ = -0.90$) and 4 ($\rho^+ = -2.20$) must indicate, however, different type of polar TS's for the homolytic cleavages in Schemes 1 and 2. Unlike the case of the ionizations of the cumyl chlorides,[27] the present polar TS[18,28] could occur due to the electronegativity difference[18] and conjugation[28] with the adjacent phenyl ring, both of which are kinetic entities and unrelated with the reactant and the product. The polarization could be accordingly classified as a sort of "imbalance",[13] and the TS is amenable to the perpendicular effect.[8] The presence of the perpendicular effect invalidates the two-dimensional reaction profile and disrupts the LHP[4,5] for the reactivities listed in Tables 1 and 4, where the kinetic and thermodynamic substituent effects are not parallel with each other to entail the dual substituent effects ($\Delta\Delta G^\ddagger_{Y\text{-}H} \neq \alpha\Delta\Delta G^\circ_{Y\text{-}H}$). The dualism might be also rationalized by Marcus theory [$\Delta G^\ddagger = \Delta G_0^\ddagger + \Delta G^\circ/2 + (\Delta G^\circ)^2/16\Delta G_0^\ddagger$].[11,12] Compared to sigma dot ($\sigma^\bullet$),[29] sigma plus (σ^+)[27] varies remarkably to bring about correspondingly notable variations of the intrinsic barrier ($\Delta G_0{}^\ddagger{}_Y$) for the polar TS. The intrinsic barriers ($\Delta G_0{}^\ddagger{}_Y$) are therefore not constant for the reactions of Schemes 1 and 2, and the corresponding $\Delta G^\ddagger_Y$ could be determined by both $\Delta G_0{}^\ddagger{}_Y$ and ΔG°_Y to prohibit the linear relation between the rate and the equilibrium.

Solvent Interactions for the Oxygen Radicals. Solvent effects in hydrogen abstractions and β-elimination by *tert*-butoxy radical[21,23] have been well established from product studies. Dipolar solvation was suggested to decrease the rate of hydrogen

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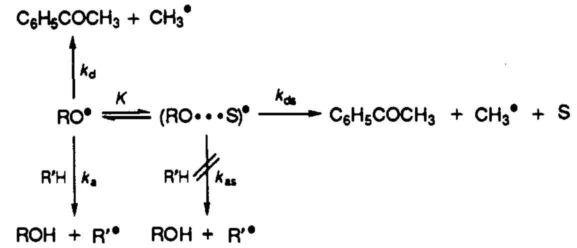
Scheme 3[a]



[a] Key: RO•, cumyloxy radical; (RO···S)•, solvated cumyloxy radical; S, solvent; R'H, cyclohexane; ROH, 2-phenyl-2-propanol; *K*, equilibrium constant; k_a and k_{as}, rate constants for the abstractions by solvent-free and solvated cumyloxy radicals, respectively, with k_{as} negligibly small; k_d and k_{ds}, rate constants for the β-scissions with solvent-free and solvated cumyloxy radicals, respectively.

abstraction relative to β-elimination. Very recently laser flash photolysis techniques[24] were employed for the same reactions of cumyloxy radical in various media. To our surprise, the rates of fragmentation become larger while those of hydrogen abstraction remain constant with increasing solvent polarity.

These observations,[23,24] at a glance, might appear incompatible but could be, nonetheless, reconciled with the equilibration between solvent-free and solvated cumyloxy radicals, where the former either abstracts hydrogen or goes through β-cleavage, while the latter solely undergoes fragmentation (Scheme 3). The ratio of the products, i.e. 2-phenyl-2-propanol and acetophenone, can be equated with eq 3.

$$\frac{\Delta[\mathrm{ROH}]}{\Delta[\mathrm{C_6H_5COCH_3}]} = \frac{k_a[\mathrm{RO}^\bullet][\mathrm{R'H}]}{k_d[\mathrm{RO}^\bullet] + k_{ds}[(\mathrm{RO}\cdots\mathrm{S})^\bullet]} \qquad (3)$$

Strong solvation of cumyloxy radical could render $k_{ds} \gg k_d$[24] and $[(\mathrm{RO}\cdots\mathrm{S})^\bullet] \gg [\mathrm{RO}^\bullet]$, whereby eq 3 could be approximated to eq 4. The yield of the alcohol is thus controlled by an equilibrium constant *K*, which is variable with solvents leading to *important solvent effects on the hydrogen abstraction reactions*. The effective rate constants of hydrogen abstraction calculated from the product studies[23] correspond thereby to k_a/K in eq 4.

$$\frac{\Delta[\mathrm{ROH}]}{\Delta[\mathrm{C_6H_5COCH_3}]} = \frac{k_a[\mathrm{RO}^\bullet]}{k_{ds}[(\mathrm{RO}\cdots\mathrm{S})^\bullet]}[\mathrm{R'H}] = \frac{k_a}{k_{ds}}\frac{1}{K}[\mathrm{R'H}] \qquad (4)$$

Walling and Wagner[23] proposed that only weakly solvated *tert*-butoxy radicals should be capable of hydrogen abstraction although at the slower rate, which must be kinetically equivalent to eq 4 with equilibration regulating the concentration of solvent-free *tert*-butoxy radical, the sole hydrogen abstractor. The photolytic studies[24] dealt with, however, solvated cumyloxy radicals only while the equilibration suggests two different states of cumyloxy radicals during the reactions. Further investigations are required to clarify these ambiguities.

Compared to *tert*-butoxy[21,23] and cumyloxy[24] radicals, the carbinyloxy radicals[20] may be dominantly stabilized via fragmentation due to the presence of two benzyl groups. As shown in Table 3, numerous solvents fail to alter relative rates of fragmentation, although serious interactions have been reported for β-cleavages of cumyloxy radicals.[24] The levelling-off of substituent effect with variation of solvent could suggest that the fragmentations may take place far before the carbinyloxy radicals experience solvations, that is, only solvent-free carbinyloxy radicals fluorish prior to the β-cleavages.

Conclusions

When the homolytic reactions traverse a polar TS, the reactivities are subject to a significant entropic contribution, which may be closely related to the perpendicular effect.[8] The two-dimensional reaction profile cannot therefore accommodate the trends of the rates, which disobey the LHP[4,5] and RSP.[6] The intramolecular fragmentation occurs much faster than the intermolecular solvation.

Experimental Section

Materials. The reagents are commercially available from major suppliers. Liquids were fractionally distilled, and solids were recrystallized according to standard procedures.[30]

Benzyl Methyl Substituted-Benzyl Carbinols were prepared via a Grignard intermediate[31] employing the same quantities of benzyl chlorides (0.1 mol) and phenylacetone (0.1 mol) with 60~70% yields. The liquid products were purified by column chromatography (on silica gel 60 from Merck with *n*-hexane/EtOAc, 9:1) to give the following ^{1}H NMR data.

^{1}H NMR data for the carbinols ($CDCl_3$ with 1% TMS)

Y	^{1}H NMR data
p-OCH_3	δ 1.0 (s, 3), 1.50 (s, 1), 2.73 (s, 4), 3.70 (s, 3), 6.70–7.20 (m, 9)
p-CH_3	δ 1.0 (s, 3), 1.40 (s, 1), 2.30 (s, 3), 2.76* (s, 4), 6.90–7.40 (m, 9)
p-F	δ 1.0 (s, 3), 1.63 (s, 1), 2.70* (s, 4), 6.70–7.20 (m, 9)
p-Cl	δ 1.0 (s, 3), 1.46 (s, 1), 2.70* (s, 4), 6.90–7.40 (m, 9)
m-Cl	δ 1.0 (s, 3), 1.43 (s, 1), 2.73* (s, 4), 6.90–7.30 (m, 9)

* Broad single peak.

Benzyl Methyl Substituted-Benzyl Carbinyl Hypochlorites were derived from the corresponding carbinols with NaOCl by the known method.[32] All the procedures were essentially the same unless otherwise stated. The carbinols were dissolved in tetrahydrofuran before they were added to bleach solution together with glacial acetic acid. After reaction, the yellow organic layer was extracted with ethyl ether two times; the combined organic layers were washed with 10% aqueous sodium carbonate, brine solution, and distilled water, in that order, and then dried over $MgSO_4$. The ether solution underwent evaporation with a rotary evaporator at room temperature to give the pure hypochlorites, whose purities were checked (>98%) by iodometric titrations. All the workups were done in the dark (mostly at night) due to the extreme photosensitivities of the hypochlorites.

1-Aryl-2,3-diphenylpropan-2-ols. The same procedure was used as with the previous studies[22] employing the Grignard method, where equimolar benzyl chloride (0.1 mol) and deoxybenzoin (0.1 mol) were reacted to give ca. 10~20% yields of the alcohols. The liquid product was purified on silica gel 60 from Merck with *n*-hexane/EtOAc, 9:1, to show the forthcoming ^{1}H NMR spectra.

^{1}H NMR data for the alcohols ($CDCl_3$ with 1% TMS)

Y	^{1}H NMR data
p-CH_3	δ 1.8 (s, 1), 2.4 (s, 3), 3.2 (m, 4), 6.8–7.4 (m, 14)
p-F	δ 1.8 (s, 1), 3.2 (m, 4), 6.8–7.4 (m, 14)
p-Cl	δ 1.8 (s, 1), 3.2 (m, 4), 6.8–7.4 (m, 14)

Photolyses of the Hypochlorites. A typical procedure was as follows. The hypochlorite (0.07 mol), chlorobenzene (0.05 mol), and trichloroethylene (0.08 mol) were diluted with a solvent in a 10-mL volumetric flask. The mixture (2 mL) was transferred to an ampule containing anhydrous K_2CO_3. After degassing and sealing, the tube underwent photolysis with a 40-W incandescent bulb for 1 half-life of the hypochlorite. The tube was then quenched with ice–water in the dark and opened for treatment with saturated $NaHSO_3$ solution to destroy remaining

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(30) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, U.K., 1980.

(31) Moore, J. A.; Dalrymple, D. L. *Experimental Methods in Organic Chemistry*; Saunders: Philadelphia, PA, 1971; Chapter 18.

(32) Mintz, M. J.; Walling, C. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, pp 184.

hypochlorite. The organic layer was dried over $MgSO_4$ and analyzed by GLC.

Oxidations of 1-Aryl-2,3-diphenylpropan-2-ols with CAN. The procedure was exactly the same as that for the previous studies. Refer to the Experimental Section of ref 22a.

Analytical Procedure. Benzyl chlorides were analyzed by GLC using a Varian Vista 4600 equipped with a flame ionization detector. The columns were of 6-ft lengths of $^1/_8$-in. tubing packed with 10% SE 30 or 15% FFAP on Chromosorb W depending upon the system to be analyzed. The chromatographic resolutions were optimum with temperature programming from 80 to 220 °C. Benzyl phenyl ketones were monitored for benzylic protons by ^{1}H NMR at 300 MHz.

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