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Induced Thermolysis of *tert*-Butyl Phenylperacetates by Thiophenol: Simultaneous Occurrence of Homolysis and Single Electron Transfer[†]

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Thermolysis of *tert*-butyl phenylperacetates in the presence of thiophenol takes place via dual mechanism. The two-bond homolysis indicates $\rho_{\mathrm{H}}^{+} = -1.16$, testifying to polar transition states. The single electron transfer yields a radical anion intermediate which undergoes fragmentation with $\rho_{\mathrm{ET}} = 1.01$.

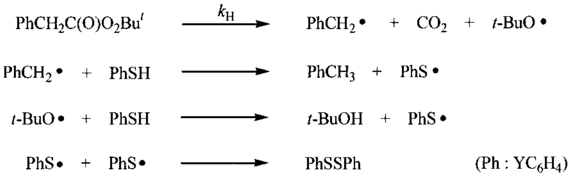
Introduction

Benzoyl peroxide[1−3] and *tert*-butyl perbenzoates[4] exhibit *fast* decompositions in the presence of nucleophiles including sulfides. 1,2-Dioxetanes[5] were reduced to corresponding vicinal diols by various thiols. The thermolysis[1−5] followed second-order kinetics, first-order in peroxidic substrate and in electron donor, respectively. We wish to herein report the reactions of ring-substituted *tert*-butyl phenylperacetates (TBPA) with thiophenol that involve concurrent homolysis and a single electron transfer (SET) mechanism.

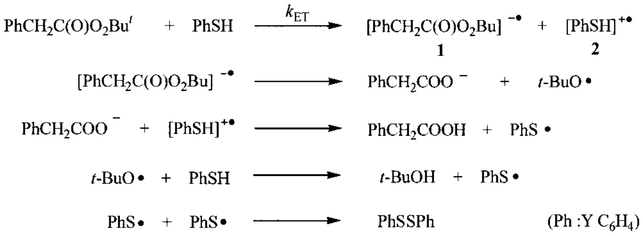
Results and Discussion

Reactions at 80 °C of degassed and sealed Pyrex tubes containing TBPA (0.05 M), thiophenol (0.5−3.5 M), bibenzyl (0.01 M, internal standard), and potassium fluoride (acid scavenger: 50 mg) in $CDCl_3$ gave rise to formations of phenylacetic acid, *tert*-butyl alcohol, toluene, and phenyl disulfide. Scheme 1 shows the two-bond homolysis of TBPA which has been thoroughly investigated by Bartlett et al.[6] and us.[7] The initial transfer of an electron from thiophenol to TBPA results in formations of the radical anion **1** and the radical cation **2**, which eventually yield phenyl acetic acid and *tert*-butyl alcohol (Scheme 2). Alternatively, they might decompose to give $PhCH_2^{\bullet}$, CO_2, and t-BuO^{-} via two-bond homolysis,[6,7]and $PhCH_2CO_2^{\bullet}$ may not intervene the reactions at all.

Scheme 1



Scheme 2



The rates of decompositions of TBPA in the presence of thiophenol can be written as with eq 1. k_{H} corresponds to rate constant for unimolecular homolysis while k_{ET} is second-order rate constant for SET reactions. Equation 1 could be transformed into a simpler form of eq 2 when a large excess (relative to concentration of TBPA) of thiophenol is utilized. Integration of eq 2 produces $\ln C_o/C = k_{\mathrm{obsd}}t$ where C_o and C denote the initial and final mole concentrations of TBPA, respectively. Ring-substituted TBPA ($YPhCH_2C(O)O_2Bu^t$, Y: p-CH_3, H, p-Cl, m-Cl, and p-NO_2) were heated at 80 °C with several different concentrations of thiophenol. The values of C_o and C were determined by NMR technique for $\ln C_o/C = k_{\mathrm{obsd}}t$. Accordingly k_{obsd} has been obtained from the plot of $\ln C_o/C$ vs t. All the plots showed good to excellent linearities with correlation coefficients $r = 0.990$ in most cases, where the slopes correspond to magnitude of k_{obsd}. Then, k_{H} and k_{ET} were determined from plot of $k_{\mathrm{obsd}} = k_{\mathrm{H}} + k_{\mathrm{ET}}[\mathrm{PhSH}]$. These plots are presented in Supporting Information. The rate data are shown with Table 1.

$$-\mathrm{d[TBPA]/dt} = k_{\mathrm{H}}[\mathrm{TBPA}] + k_{\mathrm{ET}}[\mathrm{TBPA}][\mathrm{PhSH}] \quad (1)$$

$$-\mathrm{d[TBPA]/dt} = (k_{\mathrm{H}} + k_{\mathrm{ET}}[\mathrm{PhSH}])[\mathrm{TBPA}] = k_{\mathrm{obsd}}[\mathrm{TBPA}] \quad (2)$$

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Table 1. Rate Data for Thermolysis of Ring-Substituted *tert*-Butyl Phenylperacetates with Thiophenol at 80 °C in $CDCl_3$

substituent (Y)	$k_{obsd}{}^{a} \times 10^4$, s^{-1}	$k_H{}^{b} \times 10^4$, s^{-1}	$k_{ET} \times 10^4$, s^{-1} M^{-1}
p-CH_3	2.65(0.932), 2.68(0.976) 2.76(1.516), 2.80(1.899)	2.53 ± 0.03 (2.63)	0.15 ± 0.02
p-H	1.38(1.10), 1.51(1.661) 1.66(2.377)	1.14 ± 0.01 (1.06)	0.219 ± 0.006
p-Cl	1.35(1.514), 1.41(1.744) 1.72(2.517), 1.96(3.459)	0.87 ± 0.06 (0.84)	0.32 ± 0.02
m-Cl	0.76(0.631), 1.06(0.989) 1.40(1.785), 1.57(2.068)	0.47 ± 0.07 (0.42)	0.53 ± 0.05
p-NO_2	0.938(0.519), 1.18(0.723) 1.63(1.143), 2.03(1.414) 3.09(2.074)	0.16 ± 0.01 (0.16)	1.38 ± 0.08
		$\rho_H^+ = -1.16(0.997)$ $\rho_H = -1.53(0.947)$	$\rho_{ET} = 1.01(0.996)$ $\rho_{ET}^+ = 0.89(0.992)$

[a] The figures in parentheses indicate mole concentrations (M) of thiophenol employed. [b] The values in parentheses are the rate constant (k_H) reported by us with iodine trapping of the intermediate radicals of ref 7. The two figures show an excellent agreement.

Table 2. Ratio of k_{ET}/k_H Calculated from the Yield of Toluene and Phenylacetic Acid from Themolysis of *tert*-Butyl Phenylperacetate with Thiophenol at 80 °C in $CDCl_3$

[PhSH], M	[$PhCH_3$]	[$PhCH_2CO_2H$]	k_{ET}/k_H
1.20	0.0771	0.0181	0.196
1.41	0.1048	0.0303	0.205
1.99	0.0371	0.0151	0.204

$\rho_H^+ = -1.16$ can be excellently compared with our[7] $\rho_H^+ = -1.18$ at 80 °C, considering the different reaction conditions. The negative value of ρ_H^+ indicates the polar transition state involved with the two-bond homolysis. Formation of radical anion **1** and cation **2** could be a rate-determining electron transfer. Fragmentation of **1** gave rise to phenylacetate anion and *tert*-butoxy radical. Phenylacetic acid is formed from the acetate anion and thiophenol radical cation. The magnitude of k_{ET} increases with electron-withdrawing groups to give $\rho_{ET} = 1.01$. The SET mechanism shows better correlation with σ rather than σ^+, indicating the negative charge is localized. The size of $\rho_{ET} = 1.01$ could be also consistent with SET. S_N2 reactions[8] are rather immune to electronic effect of substituent because requirements of bond formation and cleavage are opposite. Therefore, much smaller Hammett ρ value occurred. The value of k_{ET}/k_H for decomposition of $C_6H_5CH_2C(O)O_2Bu^t$ is measured to be 0.219/1.14 = 0.192 (Table 1). However, k_{ET}/k_H can be also obtained from the ratio of k_{ET} [C_6H_5SH]/k_H = [$C_6H_5CH_2CO_2H$]/[$C_6H_5CH_3$] when the perester is completely decomposed for 5 half-life. The molar concentration of toluene and phenylacetic acid were measured at 1.20, 1.41, and 1.99 M of thiophenol. The figures of k_{ET}/k_H (0.196, 0.205, and 0.204) (Table 2) is very close to $k_{ET}/k_H = 0.192$ that is obtained by measuring the disappearance of the perester (Table 1).

Formation of phenylacetic acid might be also realized via S_N2 reaction. *tert*-Butyl phenylperacetate were heated at 80 °C with variable concentrations of thiophenol in 5% $CH_3OH/CDCl_3$. The comparison is made for decomposition of the perester in pure $CDCl_3$ and 5% $CH_3OH/CDCl_3$ (Table 3). k_{ET} is accelerated and k_H is nearly identical when 5% CH_3OH is added. The acceleration of 6.08/0.219 = 27.7 can be due to the increase of polarity of the solvent that may stabilize the radical anion and cation. However, the rate should be slower by addition of CH_3OH if the reaction were to follow S_N2.

Table 3. Difference of k_{ET} Occurring with Different Solvent Systems

solvent	$k^a_{obsd} \times 10^4$, s^{-1}	$k_H \times 10^4$, s^{-1}	$k_{ET} \times 10^4$, s^{-1} M^{-1}
5% $CH_3OH/CDCl_3$	5.51(0.74), 7.50(1.027) 9.39(1.375)	1.09	6.08
$CDCl_3$	1.38(1.10), 1.51(1.661) 1.66(2.377)	1.14	0.219

[a] The figures in paretheses correspond to mole concentration of thiophenol (M) where the perester was decomposed.

Conclusion

tert-Butyl phenylperacetates interact with thiophenol via SET to give radical ion pair. The radical anion of the perester fragments into phenylacetate anion and *tert*-butoxy radical. Phenylacetate anion and thiophenol radical cation give phenylacetic acid. *tert*-Butoxy radical abstracts hydrogen from thiophenol to yield *tert*-butyl alcohol. It is interesting to note that k_H decreases but k_{ET} becomes larger when the substituent becomes electron-withdrawing. The former (k_H) is better correlated with σ^+ while the latter (k_{ET}) is with σ.

Experimental Section

Materials and Methods. Substituted phenylacetic acid, *N*,*N'*-carbonyldiimidazole, *tert*-butyl hydroperoxide, and other reagents were purchased from the major suppliers. Liquids were distilled with center-cut collection, and solids were purified according to standard procedures[9] if necessary. A Varian Gemini 2000 NMR spectrometer was used for the analysis of the reaction mixtures. *tert*-Butyl phenylperacetates ($YC_6H_4CH_2CO_3Bu^t$, Y = *p*-CH_3, *p*-H, *p*-Cl, *m*-Cl, *p*-NO_2) were prepared according to the method described in Experimental Section of reference 7.

Thermal Reactions of *tert*-Butyl Phenylperacetates. Weighed samples of a perester (0.05 M), thiophenol (0.5−2.5 M), bibenzyl (0.01 M, internal standard), and potassium fluoride (50 mg) were dissolved in $CDCl_3$ (5 mL). The solutions were divided into several Pyrex ampules that were degassed and sealed by freeze−pump−thaw method. The ampules (i.d. 4 mm, length 3 cm, 2/3 full) were immersed in a constant-temperature bath at appropriate temperature. Less than 20 s were required for complete thermal equilibration, which was measured by a copper−constantan thermocouple. At various intervals, the tubes were removed from the oil bath, quenched in ice−water, and opened. The reaction mixture was filtered and ready for NMR analysis of the remaining perester. Disappearance of the benzylic peak (δ = 3.6−3.7 ppm) was monitored. Rate constants were then calculated by the method

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of least squares, utilizing ln $C_o/C_t = k_{obsd}t$. Accordingly k_{obsd} has been obtained from the plot of ln C_o/C vs t. k_H and k_{ET} can be calculated with $k_{obsd} = k_H + k_{ET}$ [PhSH]. These are indicated in the Supporting Information.

Complete Thermal Reactions of *tert*-Butyl Phenylperacetates. Samples of *tert*-butyl phenylperacetate (0.05 M), thiophenol (1.20, 1.41, 1.99 M), and bibenzyl (0.005 M) were placed into a 2 mL volumetric flask, and $CDCl_3$ was added to the line. This solution and KF (30 mg) were divided into the ampules that subsequently underwent degassing three times and sealing. After reaction, few drops of trifluoroacetic acid were added to destroy the complex of $C_6H_5CH_2COOH{\cdot}KF$. The filterate was then analyzed with NMR for phenylacetic acid (benzylic: $\delta = 3.6-3.7$), bibenzyl (methylene: $\delta = 2.9$), *tert*-butyl alcohol (*tert*-butyl: $\delta = 1.26$), toluene (methyl: $\delta = 2.31$).

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Supporting Information Available: Graphical plots of ln C_o/C_t vs t and $k_{obsd} = k_H + k_{ET}$ [PhSH] are provided to show the accurate measurements of the rate constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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