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Hydrogen Abstractions from Thiophenols by Benzoyloxy Radicals[†1,2]

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Benzoyloxy radicals derived from benzoyl peroxide (BP) may either abstract hydrogens from substrates or add to double bonds.[3,4] The former reaction was rarely[5] investigated, while the latter has received much attention. Walling and Azar[6] studied hydrogen abstractions by benzoyloxy radicals from substrates having C–H bonds of various kinds. They compared relative rates of hydrogen abstraction using decarboxylation of benzoyloxy radical[7,8] as a standard. We now report relative reactivities of thiophenols toward benzoyloxy radicals and rationalize the results in terms of a polar transition state (TS).

Results and Discussion

Thermolyses of thiophenols with BP[9] in chlorobenzene gave benzoic acid, benzene, and phenyl disulfides as the sole major products showing excellent material balances for all runs.[10] Low concentrations of BP (5×10^{-3} M) and relatively high reactivities[34] of thiophenols at the concentrations can efficiently prevent induced and other undesirable reactions. Formations[9] of diphenyl and phenyl benzoate, both derived from in- and out-of-cage recombination, and chlorodiphenyls from the addition of phenyl radicals to the solvent were not observed at all for all reactions except for those of thiophenol, in which less than 1% formation of diphenyl, based on the quantity of BP decomposed, was detected plausibly because of its viscosity. Control experiments also indicate that occurrence of phenyl disulfides[12] cannot disturb the scheme proposed.

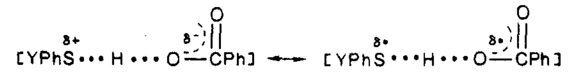
Benzoyloxy radicals may thus abstract hydrogens from thiophenols and undergo decarboxylation to give phenyl radicals, which again exclusively abstract hydrogens. Such reactions can be commonly involved with thiophenols as shown in Scheme I.

Assuming steady-state concentration for phenyl radicals, we may derive eq 5. Reactions of variable concentrations

$$\frac{[\mathrm{PhCO_2H}]}{[\mathrm{PhH}]} = k_a/k_d[\mathrm{YPhSH}] \qquad (5)$$

of each thiophenol with BP in chlorobenzene led respectively to corresponding formations of benzene and benzoic acid. Applying eq 5, plots of molar ratios of benzoic acid to benzene against the corresponding thiophenol concentrations gave straight lines with the slopes equal to k_a/k_d.[13] The rates thus obtained were fitted into the Hammett correlations which are shown in Table I and Figure 1.

A better correlation is found by using σ^+ and should accordingly imply dominence of polar TS 1, exhibiting $\rho = -1.19$. This is a well-known phenomenon for hydrogen abstractions from toluenes[14] and analogous substrates.[15-17]



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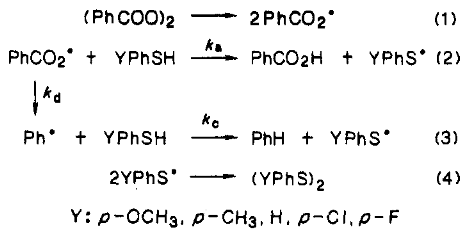
Scheme I



$$(\mathrm{PhCOO})_2 \longrightarrow 2\mathrm{PhCO_2}^{\bullet} \qquad (1)$$

$$\mathrm{PhCO_2}^{\bullet} + \mathrm{YPhSH} \xrightarrow{k_a} \mathrm{PhCO_2H} + \mathrm{YPhS}^{\bullet} \qquad (2)$$

$$\mathrm{PhCO_2}^{\bullet} \xrightarrow{k_d} \mathrm{Ph}^{\bullet}$$

$$\mathrm{Ph}^{\bullet} + \mathrm{YPhSH} \xrightarrow{k_c} \mathrm{PhH} + \mathrm{YPhS}^{\bullet} \qquad (3)$$

$$2\mathrm{YPhS}^{\bullet} \longrightarrow (\mathrm{YPhS})_2 \qquad (4)$$

Y: p-OCH$_3$, p-CH$_3$, H, p-Cl, p-F

Table I. Relative Reactivities of Thiophenols toward Benzoyloxy Radicals and the Hammett Correlations in Chlorobenzene at 100 °C

substd thiophenols[a]	k_a/k_d[b]	rel k_a
p-OCH$_3$	155.6	8.84
p-CH$_3$	40.0	2.27
p-F	22.8	1.30
H	17.6	1
p-Cl	14.1	0.80

Hammett Correlations[c,d]

$\rho(\sigma^+) = -1.19$ $r = 0.999$

$\rho(\sigma) = -1.91$ $r = 0.894$

[a] For the ranges of concentration of thiophenols, refer to Experimental Section. [b] Error limits are less than 4%, being average deviations of more than three runs. [c] σ and σ^+ were taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 334. [d] r, correlation coefficient.

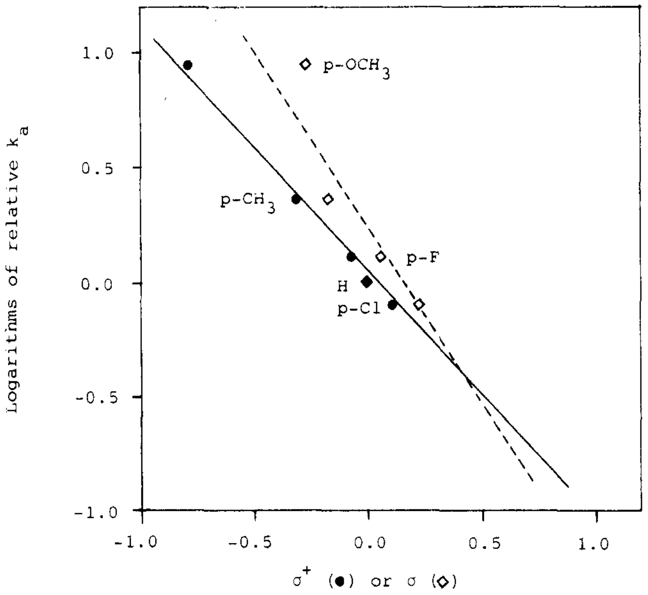


Figure 1. Hammett correlations for hydrogen abstractions from thiophenols by benzoyloxy radicals in chlorobenzene at 100 °C.

The polar substituent effect[18] was first rationalized by Russell[19] ascribing the polarity to the electron affinity and the heats of reaction. The polar concept was once criticized[20] but further advocated[21] for in terms of the thermoneutrality and the polarizability. Recently we[14] and

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[†] Dedicated to Professor Cheves Walling on the occasion of his 71st birthday.

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(2) We deeply thank the reviewer for his enlightening comments on the manuscript.

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others[22] recognize the importance of entropic term for the rates, which is mainly derived from translations[14,23] of the activated complex.[24] The $\rho(\sigma^+) = -1.19$ at 100 °C may be comparable to $\rho(\sigma^+) = -0.9$ at 22 °C for hydrogen abstractions from phenols by *tert*-butoxy radicals,[15] and $\rho(\sigma^+) = -1.04$ at 30 °C for the β-scissions of tertiary alkoxy radicals.[25] These relatively large figures may not be *fully* understood by the Russell's terms[19] alone. We may also note the β-scissions can gain remarkable translational entropies during the activation. Comparable polar effects were observed with hydrogen abstractions from toluenes by bromine atoms, $\rho(\sigma^+) = -1.40$ at 80 °C,[14,26] and by thiyl radicals, $\rho(\sigma^+) = -1.80$ at 80 °C,[27] and attributed to the polarizabilities[28] of attacking radicals.[27] Polarizabilities of the hydrogen donor and attacking radical were shown to alleviate activation energies for hydrogen abstractions.[29] Hydrogen abstractions from 4-methyl-1-phenyl-4-(4-substituted-phenyl)pentanes by trichloromethyl radicals gave $\rho(\sigma) = -0.40$ at 70 °C. The abstractions may be preceded by complexation of the radicals with the phenyl ring.[30] Entropy control of reactivity of addition of arylhalocarbenes to alkenes[23] may be reasonably influenced by such polarizabilities.

The ρ–σ^+ correlations for the hydrogen abstractions hitherto observed may seem to have one common feature, i.e., hydrogen-transferring atoms (X), whether X is carbon, oxygen, or sulfur, are adjacent to a phenyl ring having easily polarizable π-electrons. When X–H bonds begin to cleave (Ph–X···H···Z), X may develop its p orbital and the π-electrons from the phenyl ring can reside on it via conjugation, which could be further relayed to the attacking radicals ($Z^\bullet$), forming the polarity. The amount of charge-transfer may not necessarily require equivalent degree of X–H bond-breaking and instead depend upon the polarizabilities of involved groups, i.e., phenyl ring and X and Z atoms. The reactivities of hydrogen abstractions may therefore be determined by complex interplay of various elements including the polarizabilities. We may wish the theoreticians to do the same calculations on the system of hydrogen abstractions as has been done for cyclopropanations.[31]

The charge transfer can be also substantiated by forthcoming considerations. The positive charge on the sulfur atom[32] can be easily dispersed into the phenyl ring, which is indicated by the much better correlation coefficient with σ^+, $r = 0.999$, than with σ, $r = 0.894$ (factor a). The carboxylate anion is also stabilized by two canonical structures (factor b). These mesomeric charge dispersions of both ions can significantly weaken the ionic attraction. The absolute rate theory[24] tells that vibration of YPhS–H is replaced by the translation of activated complex during the activation. The translational motion may accompany large[33] entropy increase, which could be well preserved due to the weak attraction (factor c). The charge dispersions by factors a and b should lower activation enthalpies when the "looseness"[14,23] caused by c can accompany increase of the entropies, thus effectively enhancing the reactivities to give $1.13 \times 10^6 \ll k_a \le 1.8 \times 10^7$ M^{-1} s^{-1} for thiophenol.[34]

Experimental Section

Materials. All the reagents are commercial materials which were checked by GLC for purity and purified by appropriate methods if necessary. Benzoyl peroxide was recrystallized from chloroform–methanol, purity titration >99%.

Kinetic Experiments. All the experiments were carried out in homogeneous systems, consisting of substituted thiophenol, benzoyl peroxide (5×10^{-3} M), internal standard (naphthalene or dichlorobenzene, 5×10^{-3} M), and solvent (chlorobenzene). [The concentrations of thiophenols were as follows: *p*-chloro- and *p*-fluorothiophenol, 0.4–0.6 M; *p*-methoxy- and *p*-methylthiophenol, 0.1–0.25 M; thiophenol, 0.05–0.2 M.] These were placed

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(10) The molar ratios of benzoic acid plus benzene to BP were always 2.0 ± 0.05 for *all* runs, indicating the hydrogen abstractions from thiophenols as the sole sinks for benzoyloxy and phenyl radicals. In case of thiophenol, the ratio was BP/(benzoic acid + benzene)/phenyl disulfide = 1:(2.0 ± 0.05):(0.97 ± 0.04). Phenyl disulfides were not positively identified for the reactions of substituted thiophenols but tentatively assigned for by GLC retention time comparison. The patterns of GLC chromatograms were basically similar to those for reactions of thiophenol only with the difference of retention times of phenyl disulfides. The ratio of (2.0 ± 0.05) may thus validate Scheme I for all reactions. We estimate[34] k_a for

$$\mathrm{PhSH} + \mathrm{PhCO_2^\bullet} \xrightarrow{k_a} \mathrm{PhCO_2H} + \mathrm{PhS^\bullet}$$

to be $1.13 \times 10^6 \ll k_a \le 1.8 \times 10^7$ and k_c for

$$\mathrm{PhSH} + \mathrm{Ph^\bullet} \xrightarrow{k_c} \mathrm{PhH} + \mathrm{PhS^\bullet}$$

can be even larger than k_a because bond energy[11] of C_6H_5–H (BDE, 110 kcal mol^{-1}) is larger than that of $C_6H_5CO_2$–H (BDE, ≤106 kcal mol^{-1}). Such high reactivities (k_a and k_c) of thiophenols at the present concentrations can render reactions 2 and 3 fast enough to retard other less reactive reactions.

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$$\mathrm{PhSH} + \mathrm{PhCO_2^\bullet} \xrightarrow{k_a} \mathrm{PhCO_2H} + \mathrm{PhS^\bullet}$$

is calculated to be $k_a \le 1.8 \times 10^7$ M^{-1} s^{-1}. Franz et al.[35] reported $k_b = 3.13 \times 10^5$ M^{-1} s^{-1} for

$$\mathrm{PhSH} + \mathrm{PhCH_2^\bullet} \xrightarrow{k_b} \mathrm{PhCH_3} + \mathrm{PhS^\bullet}$$

at 25 °C, which becomes $k_b = 1.13 \times 10^6$ M^{-1} s^{-1} at 100 °C. Since bond energy[11] of $C_6H_5CO_2$–H (BDE, ≤106 kcal mol^{-1}) is much greater than that of $C_6H_5CH_2$–H (BDE, 88 kcal mol^{-1}), it should be $k_a \gg k_b$. It may therefore be $1.13 \times 10^6 \ll k_a \le 1.8 \times 10^7$ M^{-1} s^{-1}.

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together in sealed degassed Pyrex ampules prepared by freeze–pump–thaw method. The solutions were then heated at 100 °C for 2.5 h, which corresponds to five half-lives of the initiator. After reaction the tubes were quenched in ice–water and opened before GLC analyses.

Control Experiment Ruling Out Reactions of Phenyl Disulfides with Either Phenyl Radicals or BP. *p*-Chlorothiophenol (0.2 M), BP (5×10^{-3} M), and naphthalene (5×10^{-3} M; internal standard) were heated in chlorobenzene at 100 °C for 2.5 h with (2×10^{-3} M) and without addition of phenyl disulfide. The addition did not change at all the yields of benzene and benzoic acid, thus, giving invariable k_a/k_d.

Analytical Procedure. The reaction mixtures were analyzed on a 6 ft × $^1/_8$ in. stainless steel column packed with 10% OV-101 or 10% OV-17 on Chromosorb W by temperature programming from 80 to 200 °C by using Varian Vista 4600 GC equipped with FID and CDS 401 data system. Benzene and benzoic acid were separately analyzed, the latter being silylated with 1,1,1,3,3,3-hexamethyldisilazane before GLC analyses.

Analytical Method. The relative rates (k_a/k_d) for the thiophenols were obtained from the slopes of the lines attained by eq 5.

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Registry No. *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; $PhC(O)O^{\cdot}$, 1854-28-0.

[2 + 2] Cycloaddition of Dichloroketene to Allyl Ethers and Thioethers

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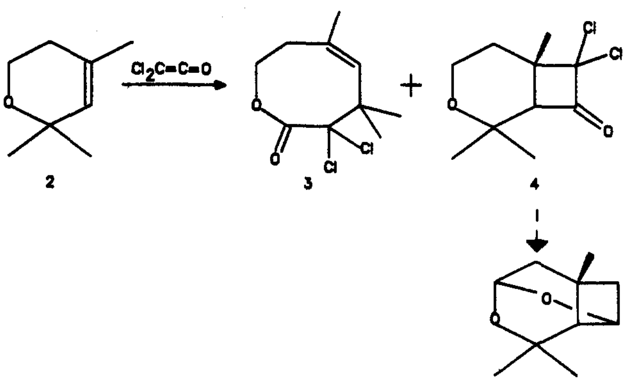
During the development of an efficient synthesis of the commercially valuable aggregation pheromone lineatin (1),[1] we investigated the addition of dichloroketene to allylic ether 2.[2] Initial experiments wherein dichloroketene was generated by dehydrohalogenation of dichloroacetyl chloride or by zinc dehalogenation of trichloroacetyl chloride gave only low yields of adducts. In the case of dehydrohalogenation route, the low yields were attributed to polymerization of dichloroketene by triethylammonium chloride[3] produced during ketene formation. This approach was abandoned after methods to circumvent this problem by slow addition of reagents[3] failed to give useful yields of adducts.

In the case of the dehalogenation route, low yields were attributed to $ZnCl_2$-induced side reactions. Sequestering of $ZnCl_2$ by addition of phosphorus oxychloride[4] gave a low yield (33% overall) of the desired [2 + 2] cycloadduct 3 (7%) and a moderate yield of the product 4 (26%) arising from rearrangement (Figure 1). Indeed, reaction of dichloroketene with allyl ethers and allyl sulfides 5 typically results in rearrangement (6) rather than [2 + 2] cycloaddition (7).[5,6] The proposed mechanism for the formation of the rearrangement product is a [3,3]-sigmatropic rearrangement of the initially formed dipolar intermediate 8. This process is presumably promoted by $ZnCl_2$. For the reaction of dichloroketene with allylic ether 2, the addition of phosphorus oxychloride did not provide sufficiently strong $ZnCl_2$ complexation to prevent its catalysis of this rearrangement. Substitution of 1,2-dimethoxyethane for phosphorus oxychloride efficiently suppressed the formation of 4, and a 50–60% yield of 3 could be realized. Optimum conditions were 4–6 equiv of 1,2-dimethoxyethane/equiv of trichloroacetyl chloride with the reaction carried out in refluxing ether for 4–5 days.



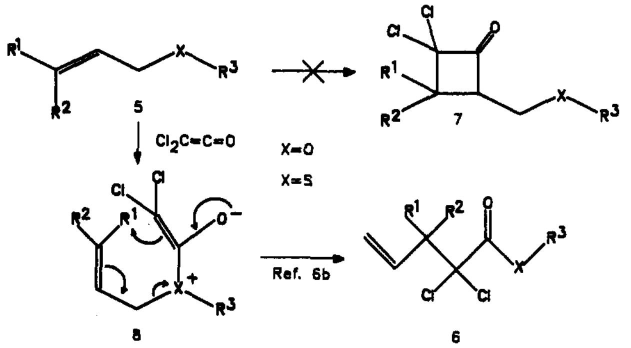


Figure 1.

In this paper, we report that the use of 1,2-dimethoxyethane as a cosolvent for [2 + 2] dichloroketene addition to allyl ethers and allyl sulfides has general utility. Addition of dichloroketene to each substrate in Table I using our modified conditions gave none of the Claisen rearrangement products. Several of these substrates have been previously shown to yield predominantly Claisen-type rearrangement products when dichloroketene was generated by the standard trichloroacetyl chloride/zinc method.[6b] For each substrate dichlorocyclobutanones were the major products. Yields of the [2 + 2] cycloadducts were, for the most part, in the range of 66–85%. Although certain of the products were unstable and tended to decompose during distillation or chromatography, dechlorination with zinc proceeded smoothly to yield the corre-

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