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Absolute Rate Constants for the Reactions of α-Toluenesulfonyl Chloride with Carbon-Centered Radicals

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The absolute rate constants for the reaction of some carbon-centered radicals with α-toluenesulfonyl chloride have been measured in solution by using laser flash photolysis techniques. At 298 K, the rate constants are 1.3 × 10^6, 1.2 × 10^6, and 1.0 × 10^8 M^{-1} s^{-1} for *n*-butyl, *sec*-butyl, and phenyl radicals respectively. Arrhenius parameters were determined for *n*-butyl and *sec*-butyl radicals. Evidence that suggests the involvement of charge-transfer interactions is presented. Such rate-enhancing interactions have been shown to have a greater influence on the preexponential factor than on the activation energy.

The key step in the radical chain decomposition of alkanesulfonyl halides[1] as well as in the adduct formation of sulfonyl halides with alkenes[2] is

$$R'SO_2X + R^\bullet \rightarrow R'SO_2^\bullet + RX$$

Kinetic data for such a reaction are very scarce; Horowitz has determined rate constants for the reaction of cyclohexyl radicals with CH_3SO_2Cl, $CH_3(CH_2)_2SO_2Cl$, and $CH_3(CH_2)_3SO_2Cl$ at 393 K, relative to the reaction with tetrachloroethylene,[3] as well as relative Arrhenius parameters in the case of CH_3SO_2Cl.[4] Iino et al. have determined chain-transfer constants of arene- and alkanesulfonyl chlorides at 333 K in styrene and methyl methacrylate polymerizations.[5] Furthermore, the relative reactivities of phenyl radicals toward *p*-toluenesulfonyl iodide, bromide, and chloride have been also reported.[6]

It has been shown recently, by two different groups using laser flash photolysis technique,[7,8] that the desulfonylation of $PhCH_2SO_2^\bullet$ occurs with an activation energy ≤5 kcal/mol;[9] if we take a "normal" Arrhenius preexponential factor,[10,11] i.e., $10^{12.0}$ M^{-1} s^{-1}, the rate constant at room temperature should be at least 2 × 10^8 s^{-1}. The rapid desulfonylation of $PhCH_2SO_2^\bullet$ makes it, in principle, a useful probe for laser flash photolytic investigation of various reactions which generate sulfonyl radicals from sulfonyl halides. For example, if radical $R^\bullet$ can be generated "instantaneously", then the measured rate constant from the growth of the benzyl radical should be equal to k_1, the rate constant for step 1.

$$\xrightarrow{\text{fast}} R^\bullet$$

$$PhCH_2SO_2Cl + R^\bullet \rightarrow PhCH_2SO_2^\bullet + RCl \quad (1)$$

$$PhCH_2SO_2^\bullet \rightarrow PhCH_2^\bullet + SO_2 \quad (2)$$

In this study we have used laser flash photolysis techniques to examine the reactivity of some carbon-centered radicals toward α-toluenesulfonyl chloride.[13]

Results

Generation of $R^\bullet$. All the results reported herein have been obtained by laser flash photolytic techniques employing either the pulse (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser or pulses (308 nm, ~4 ns, up to 80 mJ) from an excimer laser for excitation. All experiments were carried out under oxygen-free conditions, and static or flow systems were used depending on the experiments.

The reactions used as the alkyl radicals sources involve an S_H2 process[15] (eq 3–5) at the boron center of the corresponding trialkylborane.[16] Early EPR studies[17] con-

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^\bullet \quad (3)$$

$$t\text{-BuO}^\bullet + R_3B \rightarrow t\text{-BuO}\dot{B}R_3 \quad (4)$$

$$t\text{-BuO}\dot{B}R_3 \rightarrow R^\bullet + t\text{-BuOBR}_2 \quad (5)$$

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(11) An Arrhenius preexponential factor of $10^{12.0}$ s^{-1} has been obtained recently for the decarbonylation of the phenylacetyl radical ($PhCH_2\dot{C}O \rightarrow PhCH_2^\bullet + CO$).[12]

(12) (a) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531–532. (b) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529–530.

(13) The decomposition of sulfonyl chlorides initiated by radical initiators or ultraviolet light proceeds via a radical chain mechanism; on the other hand in the thermal decomposition of sulfonyl chlorides, while alkanesulfonyl chlorides would decompose by a radical chain reaction, the α-toluenesulfonyl chloride seems to decompose according to the ionic chain mechanism.[14]

(14) Thoi, H. H.; Iino, M.; Matsuda, M. *J. Org. Chem.* **1980**, *45*, 3626–3630.

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(17) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc. B* **1971**, 1823–1829.

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Table I. Kinetic Parameters for the Reactions of Some Radicals with $PhCH_2SO_2Cl$

radical	source	log A, $M^{-1}\ s^{-1}$ [a]	E_a, kcal/mol[a]	k_1, $M^{-1}\ s^{-1}$ [a,g]
$CH_3CH_2CH_2CH_2^\bullet$	n-Bu_3B[b]	10.11 ± 0.48	5.46 ± 0.35	$(1.3 \pm 0.4) \times 10^6$ [c]
$CH_3CH_2\dot{C}HCH_3$	s-Bu_3B[b]	9.62 ± 0.52	4.81 ± 0.38	$(1.2 \pm 0.3) \times 10^6$ [c]
$C_6H_5^\bullet$	PhI[d]			$(1.0 \pm 0.1) \times 10^8$
	$(PhCO_2)_2$[d]			$(0.9 \pm 0.1) \times 10^8$
$(CH_3CH_2)_3Si^\bullet$ [e]	Et_3SiH[f]			$(5.7 \pm 0.3) \times 10^9$

[a] Errors correspond to 95% confidence limits. [b] Solvent is $Me_3COOCMe_3/R_3B/C_6H_6$ (1:1:3 v/v). [c] Value derived from the complete kinetic study between 295 and 347 K, not just from the data at this temperature. [d] Solvent is Freon 113. [e] From ref 7. [f] Solvent is $Me_3COOCMe_3/Et_3SiH$ (1:1 v/v). [g] At 298 K.

cerned with rates of *tert*-butoxyl radical attack at the boron center and based on competition with hydrogen abstraction from cyclopentane give $k_4 = 1.5 \times 10^8$ and $1.5 \times 10^6\ M^{-1}\ s^{-1}$ for n-Bu_3B and *sec*-Bu_3B, respectively, at room temperature.[18] We have now found the absolute rate constante for the reaction of *tert*-butoxyl radical with *sec*-Bu_3B to be $(3.4 \pm 0.3) \times 10^6\ M^{-1}\ s^{-1}$ at 298 K by using diphenylmethanol as a probe—a technique which has been described in detail elsewhere.[19] For the above mentioned system (see eq 3–5) to be useful the alkyl radicals generation must be at least 10 times faster than their decay by reaction 1.[20] To meet, to some extent, this criterium we used [BR_3] of 1 M, because we require that $k_1[PhCH_2SO_2Cl] \geq 1 \times 10^5\ s^{-1}$ in order to work under conditions where our instrument has optimum response; we must also employ a di-*tert*-butyl peroxide concentration of at least 1 M since this compound is a poor chromophore at the excitation wavelength ($\epsilon_{337} = 0.30\ M^{-1}\ cm^{-1}$).

Reaction 5 is also required to be rapid. A recent kinetic study of the α-scission of t-$BuO\dot{B}Ph_3$ (see eq 6) yields $k_6 = 10^5\ s^{-1}$ at 298 K.[18] The α-scission of t-$BuO\dot{B}R_3$ radicals,

$$t\text{-BuO}\dot{\text{B}}\text{Ph}_3 \rightarrow t\text{-BuOBPh}_2 + \text{Ph}^\bullet \qquad (6)$$

where R = alkyl,[21] can be expected to be a more facile process as a results of the lower B–C bond dissociation energy and in agreement with the unsuccessful detection of their EPR spectra at very low temperatures.[17] Somewhat to our surprise, all the conditions required to study reaction 1 could be met for n-butyl and *sec*-butyl radicals.

The photogeneration of phenyl radicals was from both iodobenzene and benzoyl peroxide as previously described.[22]

Measurements of k_1. These measurements were carried out by monitoring the transient absorption of the benzyl radical at 317 nm.[23,24] The buildup of the signal due to the $PhCH_2^\bullet$ follows pseudo-first-order kinetics (see insert in Figure 1), which can be analyzed according to eq 7, where k_{expt} is a first-order experimental rate constant,

$$\ln \frac{A_\infty}{A_\infty - A_t} = k_{expt}t \qquad (7)$$

t is the time, A_∞ is the transient optical density in the plateau region, and A_t is the optical density at time t. The values of k_{expt} are related to the rate constants of interest according to eq 8, where k_0 is a rate constant that includes

$$k_{expt} = k_0 + k_1[PhCH_2SO_2Cl] \qquad (8)$$

all first- and pseudo-first-order processes that the alkyl or phenyl radicals undergo in the absence of substrate $PhCH_2SO_2Cl$ and that are not affected by $PhCH_2SO_2Cl$. The values of k_1 are then derived from a plot of k_{expt} vs. [$PhCH_2SO_2Cl$]. Representative examples are shown in Figures 1 and 2. Arrhenius parameters were obtained for n-butyl and *sec*-butyl radicals in the range of temperature between 295 and 347 K. All the results are summarized in Table I.

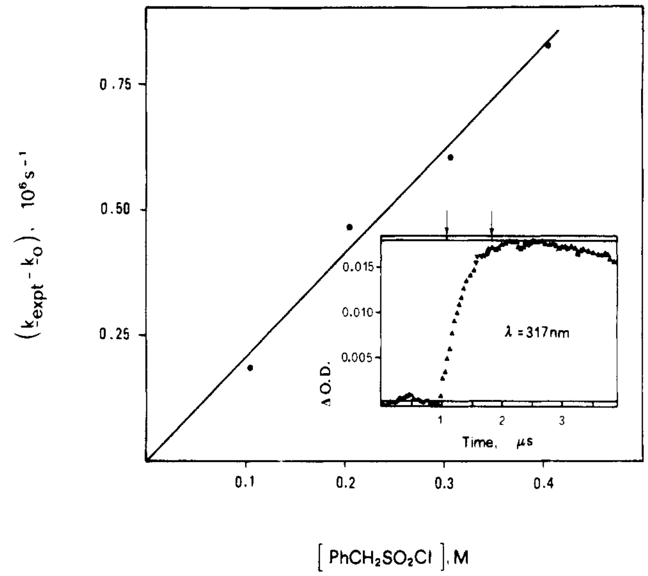

Figure 1. Plot of the experimental rate constant k_{expt} (corrected for k_0) for the reaction of the *sec*-butyl radical and $PhCH_2SO_2Cl$ at 313 K. Insert: Representative trace monitored at 317 nm for [$PhCH_2SO_2Cl$] = 0.3 M; the section between the arrows corresponds to the points used for kinetic calculations.

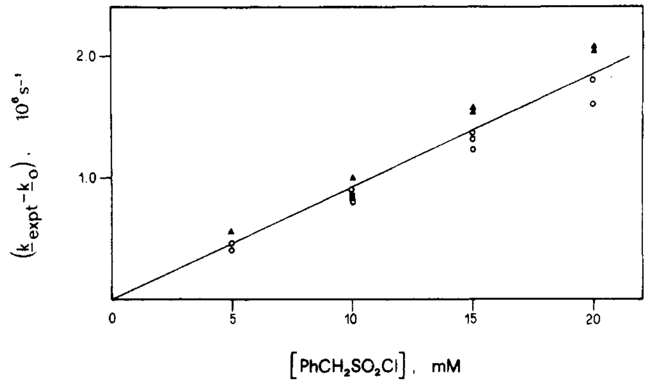

Figure 2. Reaction of phenyl radicals derived from 0.030 M of benzoyl peroxide (○) or 0.0185 M of iodobenzene (▲) with α-toluenesulfonyl chloride. Extrapolated value for [$PhCH_2SO_2Cl$] = 0 subtracted for each data point.

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(18) Griller, D.; Ingold, K. U.; Patterson, L. K.; Scaiano, J. C.; Small, R. D., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3780–3785.

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(20) While this is not an absolute requirement, systems which do not meet this criterium are poor candidates for kinetic studies.

(21) At present it is not possible to say with certainty whether t-$BuO\dot{B}R_2$ (were R = alkyl) represents a transition state or a true intermediate, that is, whether the reaction should be designated as an S_H2 (synchronous) or an S_H2 (stepwise) process.

(22) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609–3614.

(23) At which wavelength they can be readily detected ($\epsilon \approx 10000\ M^{-1}\ cm^{-1}$), see: Habersbergerová, A.; Janovský, I.; Teplý, J. *Radiat. Res. Rev.* **1968**, *1*, 109–181.

(24) See also: Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332–1335.

Table II. Kinetic Parameters (Collected from the Literature) for the Reactions of Some Radicals with CCl_4 in Solution

radical	log A, M^{-1} s^{-1}	E_a, kcal/mol	k, M^{-1} s^{-1} [a]	ref
$CH_3CH_2CH_2CH_2^{\bullet}$	8.6	5.3	5.0×10^4	33
$c\text{-}C_5H_9^{\bullet}$	7.3	4.9	5.0×10^3	33
$C_6H_5^{\bullet}$			7.8×10^6	22
$(CH_3CH_2)_3Si^{\bullet}$			4.6×10^9	32

[a] At 298 K.

Discussion

The reactivities for chlorine abstraction from $PhCH_2SO_2Cl$ are those which would be expected along the series *n*-alkyl ≈ *sec*-alkyl < phenyl < silyl. The Arrhenius parameters listed in Table I show that the preexponential factors are at least one order of magnitude larger than would generally be considered to be "normal" for free-radical abstraction, viz.,[10] $10^{8.5 \pm 0.5}$ M^{-1} s^{-1}. This implies that the transition states for these reactions, which are strongly exothermic,[25] are fairly "loose".[10] We attribute the high preexponential factors to the great importance of polar contributions to the transition state.[30] That is,

$$\underset{\mathrm{I}}{PhCH_2SO_2Cl\ {}^{\bullet}R} \leftrightarrow \underset{\mathrm{II}}{PhCH_2\dot{S}O_2Cl^-\ R^+} \leftrightarrow \underset{\mathrm{III}}{PhCH_2SO_2^-Cl^{\bullet}\ R^+} \rightarrow PhCH_2SO_2^{\bullet} + RCl \quad (9)$$

the great electron affinity of sulfonyl chlorides[31] will increase the contribution of the canonical structure with charge separation to the transition state. It has been recognized recently that polar contributions to the transition state can have a greater influence on the preexponential factor than on the activation energy.[32] Thus, the polar interactions probably relax the restriction of the colinearity of C, Cl, and S atoms in the transition state of Cl-transfer reactions.

Further evidence for such a phenomenon comes from the comparison of kinetic data for chlorine abstraction from $PhCH_2SO_2Cl$ (Table I) and CCl_4 (Table II). The high reactivity of α-toluenesulfonyl chloride relative to carbon tetrachloride cannot be attributed to more favorable thermodynamic factors. That is, the bond dissociation energies $D[PhCH_2SO_2\text{–}Cl] \simeq 71$ kcal/mol[27] and $D[Cl_3C\text{–}Cl] \simeq 70$ kcal/mol[34,35] mean that both chlorine abstractions are exothermic to the same degree for a particular radical. Thus, the difference in the reactivities of α-toluenesulfonyl chloride and carbon tetrachloride is not due to the difference in their activation energy (which arises from the enthalpies of reaction) but to the preexponential factors (cf. Arrhenius parameters for primary and secondary alkyl radicals in Tables I and II). Furthermore the statistical effects which would operate if a simple atom-transfer mechanism is assumed can increase the preexponential factor for CCl_4 relative to that for $PhCH_2SO_2Cl$ by a factor of 4 ($\sim 10^{0.6}$). We are forced to conclude that other, nonstatistical, effects are more important. In fact, the strong electron-accepting character of sulfonyl radicals may be responsible for the large contribution of the resonance form III to the $R^{\bullet}/PhCH_2SO_2Cl$ transition state (see eq 9) and consequently for increasing the reaction rate by increasing considerably the *A* factor.

Finally, our results for the *sec*-butyl radical (Table I) are in gratifying close agreement with the data of Horowitz, viz.,[4] eq 10 and 11, where $\theta = 2.303RT$ kcal/mol; $k_{10} = 2.9 \times 10^5$ M^{-1} s^{-1} at 298 K.

$$CH_3SO_2Cl + c\text{-}C_6H_{11}^{\bullet} \rightarrow CH_3SO_2^{\bullet} + c\text{-}C_6H_{11}Cl \quad (10)$$

$$\log (k_{10}/M^{-1}\ s^{-1}) = (9.07 \pm 0.17) - (4.92 \pm 0.21)/\theta \quad (11)$$

However, the small differences observed in the rate constants (a factor of 4.1 at 298 K) and in the Arrhenius parameters may be significant. In fact the increase of the rate constant from CH_3SO_2Cl to $PhCH_2SO_2Cl$ could be due to different contribution of the resonance form III (see eq 9). That is the electron-withdrawing phenyl group will stabilize the sulfinate anion on III and increase the reaction rate. A similar explanation may also be considered to apply to the very fast reactions of triethylsilyl radicals with CH_3SO_2Cl and $PhCH_2SO_2Cl$, viz.,[7] at 298 K rate constants are $(3.18 \pm 0.01) \times 10^9$ and $(5.73 \pm 0.28) \times 10^9$ M^{-1} s^{-1}, respectively.

Experimental Section

Materials. All compounds used in this work were obtained commercially and were carefully purified by standard procedures before use.

Procedure. For the reactions of *n*-butyl and *sec*-butyl radicals static experiments were carried out with samples contained in 3 mm path length rectangular quartz cells and irradiated with pulses from a Molectron UV-24 nitrogen laser.

For the reactions of phenyl radicals flow experiments were carried out in a flow system where the reaction cell was made of square (7 × 7 mm^2) quartz tubing and irradiated with pulses from a Lumonics TE-860-2 excimer laser, which was operated with Xe-HCl-He mixtures and produced pulses at 308 nm.

Technique. The laser flash photolysis apparatus used has been described in full details elsewhere.[36]

Acknowledgment. I thank Dr. J. C. Scaiano of the National Research Council of Canada for the use of the laser flash photolysis equipment and for helpful discussions and Drs. K. U. Ingold and A. S. Nazran for helpful discussions.

Registry No. *n*-Bu_3B, 122-56-5; PhI, 591-50-4; $(PhCO_2)_2$, 94-36-0; $CH_3CH_2CH_2CH_2^{\bullet}$, 2492-36-6; $CH_3CH_2C^{\bullet}HCH_3$, 2348-55-2; $C_6H_5^{\bullet}$, 2396-01-2; $PhCH_2SO_2Cl$, 1939-99-7; *sec*-Bu_3B, 1113-78-6; *t*-BuOOBu-*t*, 110-05-4; *t*-$BuO^{\bullet}$, 3141-58-0; Cl_2, 7782-50-5.

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(25) The chlorine atom abstraction from $PhCH_2SO_2Cl$ by primary alkyl, *sec*-alkyl, phenyl, and trialkylsilyl radicals are exothermic by 9, 10, 15, and 42 kcal/mol, respectively, these estimates being based on bond dissociation energies for RSO_2Cl,[26,27] CH_3CH_2Cl,[29] $(CH_3)_2CHCl$,[29] PhCl,[29] and $(CH_3)_3SiCl$[29] of 71, 80, 81, 96, and 113 kcal/mol, respectively.

(26) Wicke, E. *Ergeb. Exakten Naturwiss.* **1942**, *20*, 1; *Naturwissenschaften* **1948**, *35*, 355.

(27) The sulfur–chlorine bond dissociation energy, $D[RSO_2\text{–}Cl]$, should be virtually independent of the nature of R since there can be little or no delocalization of the unpaired electron in the sulfonyl radicals even when there is a neighboring aromatic ring.[28]

(28) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 770–775; *Ibid.* **1980**, 1429–1436.

(29) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(30) For general discussions of polar effects in radical reactions, see: Russell, G. A. *Free Radicals* **1973**, *1*, 275–331. Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* **1980**, *6*, 65–153.

(31) The electron affinity of sulfonyl chloride is still unknown up to date. However, evidence of a low-lying $\sigma_{S\text{–}Cl}{}^*$ orbital has been obtained; see: Barbarella, G.; Chatgilialoglu, C.; Rossini, S.; Tugnoli, V., submitted for publication in *J. Magn. Reson.*

(32) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123–5127.

(33) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4721–4724.

(34) *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1979–1980; Table 5, F-241.

(35) A value of 73 kcal/mol has also been estimated for this bond dissociation energy.[29]

(36) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.