THE JOURNAL OF Organic Chemistry®

VOLUME 43, NUMBER 5

MARCH 3, 1978

Relative Rate Constants for Hydrogen Atom Abstraction by the Cyclohexanethiyl and Benzenethiyl Radicals

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Received June 28, 1977

Relative values of the rate constants k (eq 1) for hydrogen atom abstraction from a number of organic substrates by cyclohexanethiyl and benzenethiyl radicals at 80 °C are reported. Good correlations with both σ and σ^+ constants were found for ring-substituted ethylbenzene and cumene derivatives, and some limited data for toluenes also are reported. Two new methods were developed to obtain these data; the key feature of both is that tritium-labeled thiol (RSH*) is used as a solvent. In this environment, reversal of the hydrogen abstraction reaction (eq 2) leads to labeling of the hydrogen donor (QH), and k is related to the radioactivity incorporated into the recovered QH*. Isotope effects are involved in the calculations, but they can be evaluated independently. Thiyl radicals are found to be extremely selective, more so than even bromine atoms or $CCl_3\cdot$ radicals. Surprisingly, both cyclohexanethiyl and benzenethiyl radicals, and also bromine atoms, show remarkably similar polar effects; this is not what would be expected on the basis of heats of reaction or electron affinities. It is suggested that this similarity might be attributable to the similar polarizabilities of bromine atoms and thiyl radicals.

Thiyl radicals are important species in organic free-radical chemistry[2-4] and in biology,[5] and their reactions are the subject of several critical reviews. Hydrogen abstraction by thiyl radicals from organic substrates is amply documented,[2a,c,d,4,5] and work by Walling and Rabinowitz[6] and by Kooyman[7] provided important qualitative and semiquantitative information. However, no quantitative data on hydrogen abstraction by thiyl radicals (eq 1) have been published.

$$RS\cdot + QH \xrightarrow{k} RSH + Q\cdot \qquad (1)$$

In a preliminary communication,[8] we reported a method for the quantitative study of eq 1 and preliminary results for the cyclohexanethiyl radical. We here present further data on the cyclohexanethiyl radical and also data on the benzenethiyl radical.

Because there were no data in the literature against which to test our method, we developed two independent techniques[8] for the determination of relative values of k. The key feature of both techniques is the use of tritium-labeled thiol (RSH*) as a solvent. In this environment, Q· radicals generated in eq 1 abstract hydrogen from labeled solvent RSH*, resulting in the substrate becoming tritium labeled (eq 2). The

$$Q\cdot + RSH^* \rightarrow QH^* + RS\cdot \qquad (2)$$

level of radioactivity in the recovered QH* is related to the specific rate constant for eq 1. Tritium isotope effects are involved in the calculation, but they can be evaluated independently.[9] Therefore, the very reversibility of eq 1, which hindered previous studies,[2a] is utilized in our kinetic technique.

Experimental Section

Materials. Purification and preparation of the materials and equipment are described in detail elsewhere.[10]

Product Studies. Products from the reaction of cyclohexanethiol with cumene were determined by GLC analysis. Low injection temperatures were necessary to prevent further reaction. The results of these experiments are shown in Table I and are discussed further in the Appendix.

Kinetic Methods. Two kinetic methods were used and it will be convenient to describe them here.

A. Competitive Method. Reaction mixtures were typically ~0.25 M in each QH and ~0.01 M in 2,2′-azobis(isobutyronitrile) (AIBN), and the specific activity of the thiol was 10^{11}–10^{12} disintegrations per minute per mole (dpm/mol). Preweighed quantities of two hydrogen donors (QH's) and AIBN were placed in a volumetric flask and dissolved in labeled thiol; aliquots of the solution were transferred to Pyrex glass ampules, which were then degassed and sealed under vacuum. The samples were allowed to react for 5 h at 80.0 ± 0.1 °C. Sample workup involved some or all of the following steps (the intervening water washings are omitted): dilution with petroleum ether or diethyl ether; extraction with 20% sodium hydroxide; addition of 10% silver nitrate and centrifugation; extraction with saturated mercuric nitrate in dilute nitric acid; drying and quick treatment with active Raney nickel. Most of the solvent was evaporated at reduced pressure, and the donors usually were separated by GLC and subsequently radioassayed.

B. Standard Reaction Method. Reaction mixtures were initially ~0.25 M in triphenyl phosphite (TPP), ~0.25 M in QH, and ~0.01 M in AIBN. Reaction times were variable (10–70 min at 80.0 ± 0.1 °C); the ampules were thermally quenched and were opened just prior to determination of cyclohexane content by GLC. Sample preparation and workup were accomplished by the procedures outlined in connection with the competitive method; the recovered donor (QH) was separated from the remaining solvent and trace impurities by GLC, and then the donor was radioassayed.

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Table I. Product Studies [a] of Reaction Mixtures Compounded with AIBN and Cumene in Cyclohexanethiol Solvent

Run	1	2	3	4	5
Reaction time,[b] h	5.0	5.0	9.62	9.62	9.62
[Cumene]$_i$	0	0.50	0	0.50	2.5
[$C_6H_{11}SH$]$_i$	8.2	7.7	8.2	7.7	5.7
[AIBN]$_i$ × 10^3	6.90	7.19	19.4	18.5	17.6
[Isobutyronitrile]$_f$ × 10^3	5.8	8.25	18.3	18.8	18.0
	(44.6)[c]	(60.8)[c]	(47.4)[c]	(51)[c]	(51.4)[c]
[Dicyclohexyl disulfide]$_f$ × 10^3	3.7	4.1	10.2	9.7	5.55
[A_2] × 10^3 [d]	1.65	2.23	4.7	4.4	4.3
	(25.3)[c]	(32.9)[c]	(24.4)[c]	(23.9)[c]	(24.6)[c]
[Bicumene]$_f$ × 10^3		0		0	~1.3
[Sulfide 2] × 10^3 [d]		0		0	~4.6
[Sulfide 1][d]		Trace[e]		Trace[e]	Trace[e]
Recovery of $C_6H_{11}S\cdot$ radicals, %[f]	127	100	112	103	101
Recovery of A· radicals, %	70	85	72	75	76

[a] Reaction temperature was 80 °C. Brackets denote concentrations in moles per liter. Subscripts i and f indicate initial and final concentrations, respectively. [b] After 5 h, 93.8% of the AIBN has reacted; after 9.62 h, 99.6% has reacted. [c] Conversion (%), based on AIBN decomposed. [d] Tetramethylsuccinodinitrile is A_2; cyclohexyl 2-(phenylpropyl) sulfide is sulfide **2**; cyclohexyl 1-methyl-1-phenyethyl sulfide is sulfide 1 (R =cyclohexyl). [e] See ref 10. [f] Assuming that the numbers of thiyl radicals and isobutyronitrile molecules formed are the same.

Tritium Activity Determination. Two different radioassay procedures were utilized: proportional gas-flow and liquid scintillation counting. Gas-flow counting was accomplished by means of a Model 4498 gas radiochromatography system from Nuclear Chicago coupled to a Varian Aerograph Model 200 gas chromatograph fitted with thermal conductivity detector and recorder. Alternatively, sample components were individually trapped by delivery of the effluent gases (as a stream of fine bubbles) into a low-potassium vial containing 15.0 mL of a toluene-based solution of liquid scintillation fluors, and each trapped component's specific activity was measured using a Packard Tri-Carb liquid scintillation spectrometer (Model 3365). Counting efficiency was determined by automatic external standardization. The component's gross activity was corrected by subtracting from it both background activity and the activity contributed by traces of radiochemical impurities that might have been collected along with the component. The latter correction was usually small, amounting to 1–5% of the gross activity; it was obtained from the net disintegration rates of the two fractions that were collected just before and after the component's peak and from the collection times of all three fractions. This "radiochemical background" per minute of collection time was taken to be the average of the net disintegration rates per minute of collection time for the leading and trailing fractions. Since values obtained by using different chromatographic columns and/or flow-counting methods agreed well with activities corrected for "radiochemical background", we feel that the correction is sufficiently accurate.

Liquid scintillation counting of thiols proved to present special problems; however, the thiols could be counted successfully if oxygen was excluded from the vial and Packard's "Permafluor" was used in toluene solution.[11a]

Measurement of Isotope Effects. Isotope effects for both thiyl radicals were measured using ethylbenzene and ethylbenzene-d_{10}. For the cyclohexanethiyl radical, ethylbenzene was compared with cumene, ethylbenzene-d_{10} with p-nitrocumene, and cumene with p-nitrocumene. For the benzenethiyl radical, ethylbenzene-d_{10} was compared with p-ethylnitrobenzene. Thus, in all cases, three ratios of rate constants were measured: QH vs. Q′H, QD vs. Q″H, and Q′H vs. Q″H. This experimental design allows both ethylbenzene and ethylbenzene-d_{10} to be compared with a substrate of roughly comparable reactivity and from which each could be easily separated by GLC.

Results

Derivation of Kinetic Expressions. We used two methods for determining the relative reactivities of hydrogen donors toward thiyl radicals. The first involves direct competition of two donors with thiyl radicals generated by the thermal decomposition of AIBN in tritiated thiol solvent. This scheme is shown in eq 3–7, where QH and Q°H are the two hydrogen

$$\mathrm{AIBN} \rightarrow 2\mathrm{A}\cdot \xrightarrow{\mathrm{RSH}} 2\mathrm{RS}\cdot \qquad (3)$$

$$\mathrm{RS}\cdot + \mathrm{QH} \xrightarrow{k} \mathrm{RSH} + \mathrm{Q}\cdot \qquad (4)$$

$$\mathrm{Q}\cdot + \mathrm{RSH(RST)} \xrightarrow{k_\mathrm{H}(k_\mathrm{T})} \mathrm{QH(QT)} + \mathrm{RS}\cdot \qquad (5)$$

$$\mathrm{RS}\cdot + \mathrm{Q^\circ H} \xrightarrow{k^\circ} \mathrm{RSH} + \mathrm{Q^\circ}\cdot \qquad (6)$$

$$\mathrm{Q^\circ}\cdot + \mathrm{RSH(RST)} \xrightarrow{k^\circ_\mathrm{H}(k^\circ_\mathrm{T})} \mathrm{Q^\circ H(Q^\circ T)} + \mathrm{RS}\cdot \qquad (7)$$

donors, and the Q· and Q°· radicals become labeled as they abstract hydrogen (tritium) from the thiol solvent. If a steady state in these substrate radicals is assumed, kinetic analysis yields eq 8. Since [RST]/[RSH] is much less than unity, and

$$\frac{k}{k^\circ} = \left[\frac{k_\mathrm{H}/k_\mathrm{T} + [\mathrm{RST}]/[\mathrm{RSH}]}{k^\circ_\mathrm{H}/k^\circ_\mathrm{T} + [\mathrm{RST}]/[\mathrm{RSH}]}\right]\left[\frac{\mathrm{d}[\mathrm{QT}]/[\mathrm{QH}]}{\mathrm{d}[\mathrm{Q^\circ T}]/[\mathrm{Q^\circ H}]}\right] \qquad (8)$$

since both $k_\mathrm{H}/k_\mathrm{T}$ and $k^\circ_\mathrm{H}/k^\circ_\mathrm{T}$ are primary kinetic isotope effects and are greater than unity, eq 8 can be simplified to give eq 9. At low conversions, the concentrations of QH and

$$\frac{k}{k^\circ} = \left[\frac{k_\mathrm{H}/k_\mathrm{T}}{k^\circ_\mathrm{H}/k^\circ_\mathrm{T}}\right]\left[\frac{\mathrm{d}[\mathrm{QT}]/[\mathrm{QH}]}{\mathrm{d}[\mathrm{Q^\circ T}]/[\mathrm{Q^\circ H}]}\right] \qquad (9)$$

Q°H remain essentially unchanged, and d[QT] and d[Q°T] may be approximated by the final concentrations of these species. Thus, eq 9 reduces to eq 10. Finally, since [QT]/[QH]

$$\frac{k}{k^\circ} = \left[\frac{k_\mathrm{H}/k_\mathrm{T}}{k^\circ_\mathrm{H}/k^\circ_\mathrm{T}}\right]\left[\frac{[\mathrm{QT}]/[\mathrm{QH}]}{[\mathrm{Q^\circ T}]/[\mathrm{Q^\circ H}]}\right] \qquad (10)$$

is proportional to the specific activity of QH (A_QH), we obtain eq 11, in which the relative rate constant for eq 4 is expressed

$$\frac{k}{k^\circ} = \left[\frac{k_\mathrm{H}/k_\mathrm{T}}{k^\circ_\mathrm{H}/k^\circ_\mathrm{T}}\right]\left[\frac{A_\mathrm{QH}}{A_\mathrm{Q^\circ H}}\right] \qquad (11)$$

as a function of kinetic isotope effects for hydrogen abstraction from labeled solvent by substrate radicals and the specific activity ratio of the two substrates after reaction.

The second method is similar, except that only one hydrogen donor is involved, and the desulfuration of thiyl radicals by triphenyl phosphite (TPP)[12] is the standard reaction. This sequence is shown in eq 12 and 13. Kinetic analysis of the

$$\mathrm{RS}\cdot + \mathrm{(PhO)_3P} \xrightarrow{k_\mathrm{P}} \mathrm{R}\cdot + \mathrm{(PhO)_3P{=}S} \qquad (12)$$

$$\mathrm{R}\cdot + \mathrm{RSH(RST)} \xrightarrow{k'_\mathrm{H}(k'_\mathrm{T})} \mathrm{RH(RT)} + \mathrm{RS}\cdot \qquad (13)$$

system comprised of eq 3–5, 12, and 13 yields eq 14. Since $[\mathrm{RST}]/[\mathrm{RSH}] \ll 1$, $k'_\mathrm{T}/k'_\mathrm{H} < 1$, and $k_\mathrm{H}/k_\mathrm{T} > 1$, and at low

Table II. Relative Rate Constants[a] for Hydrogen Abstraction by Thiyl Radicals at 80 °C (per Reactive Hydrogen)

		A_{QH}/A_{EtPh}				Rel k values (eq 1)	
Hydrogen donor	Registry no.	Cyclohexanethiyl[b]	Benzenethiyl[c]	n[d]	Isotope correction factor[e]	Cyclohexanethiyl[f]	Benzenethiyl
n-Dodecane	112-40-3	0.03		20	0.59	0.002	
Thioanisole	100-68-5	<0.063		3	1.00[g]	<0.042	
Anisole	100-66-3	0.0075		3	1.00[g]	0.005	
Ethyl *N*,*N*-dimethylaminoacetate	33229-89-9	0.02		2	1.00[g]	0.02	
2,3,4-Trimethylpentane	565-75-3	0.0435		3	0.83	0.024	
Neopentylbenzene	1007-26-7	0.0143		2	1.00	0.014	
Toluene	108-88-3	0.045		3	0.93	0.028	
m-Xylene	108-38-3	0.129[h]		6	0.93	0.040	
Mesitylene	108-67-8	0.256		9	0.93	0.053	
p-Xylene	106-42-3	0.198		6	0.93	0.061	
Ethylbenzene-d_{10}	25837-05-2	0.120	0.133	2	1.00	0.120	0.133
p-Nitroethylbenzene	100-12-9	0.371	0.396	2	1.00	0.371	0.396
p-Bromoethylbenzene	1585-07-5	0.73	0.76	2	1.00	0.73	0.76
Ethylbenzene	100-41-4	(1.00)	(1.00)	2	(1.00)	(1.00)	(1.00)
m-Ethylanisole	10568-38-4	1.10		2	1.00	1.10	
m-Ethyltoluene	620-14-4	1.25[i]		2	1.00	1.25	
p-Ethyltoluene	622-96-8	1.60[i]	1.87[i]	2	1.00	1.60	1.87
p-Ethylanisole	1515-95-3	3.01	3.53	2	1.00	3.01	3.53
Diphenylmethane	101-81-5	1.47	2.79	2	1.08	1.59	3.01
p-Nitrocumene	1817-47-6	1.19		1	1.00	2.38	
Cumene	98-82-8	3.15	4.01	1	1.00	6.30	8.02
p-Cymene	99-87-6	5.08[h]		1	1.00	10.2	
p-Methoxycumene	4132-48-3	6.91		1	1.00	13.8	
Triphenylmethane	519-73-3	8.0		1	1.11	17.8[j]	
Benzyl methyl ether	538-86-3	24.5		2	1.11	27.2	
1,2,3,4-Tetrahydronaphthalene	119-64-2		17.1	2[k]	1.00		17.1
9,10-Dihydroanthracene	613-31-0	180		2[k]	1.11	200[j]	

[a] Relative to ethylbenzene (k = 1.00). Reproducibility of these data is ±5% except for the deuterated compounds for which it is ±10%. [b] Most of these data were obtained only by the competitive method. Registry no.: 40210-86-4. [c] Determined by the competitive method only. Registry no.: 4985-62-0. [d] Number of equivalent reactive hydrogens assumed. [e] The isotope correction factor equals $(k_H/k_T)_{QH}/(k_H/k_T)_{EtPh}$; see text. [f] Multiplying these values by 1 × 10⁶ gives approximate absolute rate constants in units of $M^{-1}\ s^{-1}$; see text. [g] Assumed to be unity; no data available. [h] Determined by both methods. [i] These are the measured ratios. It is assumed that only secondary benzylic hydrogens are abstracted. [j] Perhaps low by a factor of 2; see discussion in text. [k] See ref 23b,c.

conversions d[QT] = [QT] and d[RH] = [RH], eq 14 can be reduced and rearranged to yield eq 15, where again the A values are specific activities.

$$\frac{d[QT]}{d[RH]} = \left[\frac{k[QH]}{k_P[TPP]}\right]\left[\frac{1 + (k'_T/k'_H)([RST]/[RSH])}{1 + (k_H/k_T)([RSH]/[RST])}\right] \quad (14)$$

$$A_{QH}\,[TPP] = (k/k_P)(k_T/k_H)A_{RSH}\,[RH] \quad (15)$$

A plot of A_{QH} [TPP] vs. [RH] should be linear and have a slope M that is proportional to the rate constant for hydrogen abstraction from QH by thiyl radicals. If this is done for two different QH's, eq 16a and 16b are obtained; these can be combined to yield eq 17. The relative reactivities obtained from eq 17 can be directly compared with those obtained using the first method, eq 11.

$$M_{QH} = (k/k_P)(k_T/k_H)(A_{RSH}) \quad (16a)$$

$$M_{Q°H} = (k°/k_P)(k°_T/k°_H)(A°_{RSH}) \quad (16b)$$

$$\frac{k}{k°} = \left[\frac{M_{QH}}{M_{Q°H}}\right]\left[\frac{A_{RSH}}{A°_{RSH}}\right]\left[\frac{k_H/k_T}{k°_H/k°_T}\right] \quad (17)$$

A number of control experiments were performed to test the validity of these kinetic schemes and to probe for possible failures. These experiments are discussed in the Appendix.

Relative Reactivities of Hydrocarbons toward Thiyl Radicals. Equation 11 allows the calculation of relative values of k from the ratio of specific activities of the recovered QH's and an isotope effect correction term. The values of $A_{QH}/A_{Q°H}$, where Q°H is ethylbenzene, for both cyclohexanethiyl and benzenethiyl radicals are given in the third and fourth columns of Table II, respectively. These data are on a per molecule basis. The isotope effects for hydrogen abstraction from *tert*-butyl mercaptan by a number of carbon-centered radicals have been measured;[9a,11] these values are shown in Table III. If it is assumed that these values are not substantially affected by the nature of the thiol,[9a] but only by the structure of the carbon-centered radical (primary, secondary, benzylic, etc.), then these isotope effects can be used to estimate the isotope effect correction factors $(k_H/k_T)/(k°_H/k°_T)$ required in eq 11. These estimated correction factors are listed in the sixth column of Table II. Relative values of k can then be derived by multiplying the measured activity ratios by the isotope correction factors. These relative k values, on a per hydrogen basis, are tabulated for the cyclohexanethiyl and benzenethiyl radicals in the last two columns of Table II.

Absolute Rate Constants. Absolute rate constants can be obtained for reaction 1, where RS· is the cyclohexanethiyl radical and QH is ethylbenzene, using eq 16b. For this treatment, it must be assumed that k_P has the same value[12] ($1.2 \times 10^7\ M^{-1}\ s^{-1}$ at 70 °C) for both the cyclohexanethiyl radical and the *n*-butanethiyl radical reacting with TPP. The other numerical values required are $M_{Q°H} = 7.7 \times 10^9$ dpm/mol, $(A_{RSH})_{Q°H} = 8.0 \times 10^{11}$ dpm/mol, and the primary tritium isotope effect, $k°_H/k°_T$, for hydrogen abstraction from cyclohexanethiol by 1-phenethyl radicals.[10] Assuming the value of this isotope effect is 10 (see the previous section), the absolute rate constant (per molecule) for the reaction of the cyclohexanethiyl radical with ethylbenzene is approximately $1 \times 10^6\ M^{-1}\ s^{-1}$. Using this value, all the relative k values for the cyclohexanethiyl radical in Table II can be put on an absolute basis by multiplying by 1×10^6.

Isotope Effects for Hydrogen Abstraction by Thiyl Radicals. Using ethylbenzene-d_{10}, the deuterium kinetic isotope effects for hydrogen abstraction by the two thiyl

Table III. Kinetic Isotope Effects on Hydrogen Atom Abstraction from *tert*-Butyl Mercaptan by Carbon Radicals in Solution[a]

Radical	k_H/k_T (80 °C)
3-Heptyl	5.89
Triethylmethyl	8.33
Benzyl	9.28
Diphenylmethyl	~10.8
Triphenylmethyl	11.1

[a] Taken from K. G. Kneipp, Dissertation, Louisiana State University, Baton Rouge, La., 1971. Also see ref 9a.

Table IV. Relative Rate Constants for Hydrogen Abstraction from Aralkyl Hydrocarbons by Various Radicals (per Hydrogen Atom)

	Substrate			Rxn temp,
Radical	Toluene	Ethylbenzene	Cumene	°C
Ph·	0.22	1	2.1	60[a]
CH_3·	0.22	1	3.1	65, 110[b]
Br·	0.04	1	2.3	77[c]
Cl_3C·	0.02	1	5.2	40[d]
$C_6H_{11}S$·	0.03	1	6.3	80[e]
PhS·	[f]	1	8.0	80[e]

[a] R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85,** 3754 (1963). [b] W. A. Pryor, D. L. Fuller, and J. P. Stanley, *ibid.*, **94,** 1632 (1972). [c] S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **34,** 900 (1969). [d] G. A. Russell and C. DeBoer, *J. Am. Chem. Soc.*, **85,** 3136 (1963). [e] This work. [f] The PhS· radical is not sufficiently reactive toward toluene to allow accurate determination of this value.

radicals were determined. The k_H/k_D values are 8 for both the cyclohexanethiyl and the benzenethiyl radicals. These values are probably accurate to 10%. With perdeuterated ethylbenzene as the substrate, the α- and β-deuterium atoms give rise to secondary kinetic isotope effects. However, these effects will not be of sufficient magnitude to make a significant contribution to our reported primary isotope effects.[11d]

Discussion

Table II gives relative k values (eq 1) for 26 hydrogen donors. It is satisfying that the qualitative results reported by Walling[6] and by Kooyman[6] are in reasonably good agreement with our data. Most of our results were obtained by the competitive method (eq 3–7) because it can be applied to both alkanethiyl and arenethiyl radicals and is less time consuming than the phosphite ester procedure.

Selectivity of Thiyl Radicals. The relative rate constants for the cyclohexanethiyl radical vary by 10^5 as the nature of the donor is varied. Thiyl radicals, therefore, are extremely selective in hydrogen atom abstraction reactions. For comparison purposes, Table IV gives the relative rate constants for hydrogen abstraction from toluene, ethylbenzene, and cumene by six radicals. These data show the considerable selectivity of thiyl radicals relative to other radicals that have been studied. Toward aralkyl hydrocarbons, both thiyl radicals are even more selective than are bromine atoms.[13-15] Cyclohexanethiyl is roughly as selective as the trichloromethyl radical.[16,17] The data suggest that the benzenethiyl radical is the most selective of the group.

Diphenylmethane is somewhat more reactive than ethylbenzene toward both thiyl radicals (see Table II), whereas the opposite is true for bromine atoms.[14] Russell has pointed out that, of all the common radicals and atoms, only the chlorine and bromine atoms give a reaction series in which diphenylmethane is less reactive than ethylbenzene.[18] This peculiarity of the halogen atoms can be rationalized as due to their tendency to attack sites of high electron density. The high electron affinities of the chlorine and bromine atoms (3.61 and 3.36 eV, respectively[19]) render them strongly electrophilic, and the electron-withdrawing inductive effect of a phenyl substituent deactivates benzylic hydrogens toward highly electrophilic reagents. Thiyl radicals, which are characterized by lower electron affinities than the halogens,[20] seem to follow a reactivity pattern similar to that of other nonhalogen radicals.

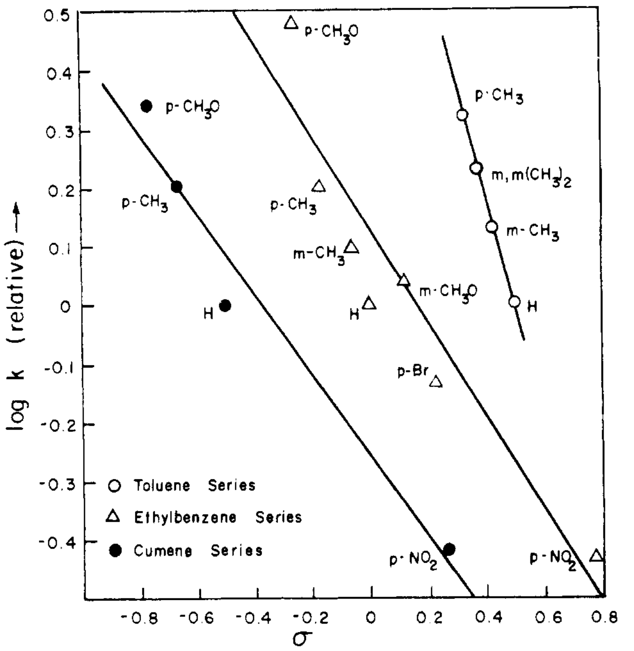


Figure 1. Hammett correlations for benzylic hydrogen abstraction by the cyclohexanethiyl radical. The σ scale has been adjusted by −0.5 for the cumene series and +0.5 for the toluene series to allow all three lines to be shown on the same plot.

The benzylic hydrogens in neopentylbenzene are less reactive than are those in ethylbenzene toward both bromine atoms and cyclohexanethiyl radicals; this probably reflects the similar steric requirements[21] of Br· and $C_6H_{11}S$· radicals.

Most stable free radicals readily abstract hydrogen from thiols;[2f,9a,22] however, triphenylmethyl radicals seem to be able to persist for relatively long time periods in the presence of thiols. Lewis[9c] reports that the reaction of triphenylmethyl dimer with excess benzenethiol in toluene solution yields phenyltrityl sulfide and triphenylmethane in equimolar amounts; diphenyl disulfide could not be detected. Thus, trityl radicals probably participate in termination reactions in our system, and this violates one of the assumptions involved in the derivation of eq 11 and 17. Therefore, our measured values of k could be up to 50% smaller for triphenylmethane than the true value; i.e., only half the trityl radicals may react with thiol and become labeled.

The high reactivity of the secondary benzylic hydrogens in 9,10-dihydroanthracene and tetralin can be compared with the lower k values for ethylbenzene or diphenylmethane, which also possess secondary benzylic hydrogens. This is quite general; peroxy, trichloromethyl, methyl, phenyl, *tert*-butoxy, chlorine, and bromine radicals behave similarly.[23]

Hammett Equation Correlations. The relative k values (Table II) for hydrogen abstraction from ring-substituted toluenes, ethylbenzenes, and cumenes by the cyclohexanethiyl radical and from ethylbenzenes by benzenethiyl radicals were correlated with both σ and σ^+ substituent parameters. (See Figures 1–3.) The results of these correlations are listed in

Table V. ρ **Values for Hydrogen Abstraction by Cyclohexanethiyl and Benzenethiyl Radicals at 80 °C**

Abstracting radical	Substrate	Solvent	No. of data points	Substituent[a] constants	ρ^b	C.L.[c]	Correlation coeff
Cyclohexanethiyl	Toluenes	Cyclohexanethiol	4	σ	−1.96	0.26	0.999
Cyclohexanethiyl	Toluenes	Cyclohexanethiol	4	σ^+	−1.00	1.21	0.900
Cyclohexanethiyl	Ethylbenzenes	Cyclohexanethiol	7	σ	−0.76	0.13	0.943
Cyclohexanethiyl	Ethylbenzenes	Cyclohexanethiol	7	σ^+	−0.59	0.07	0.990
Cyclohexanethiyl	Cumenes	Cyclohexanethiol	4	σ	−0.69	0.41	0.980
Cyclohexanethiyl	Cumenes	Cyclohexanethiol	4	σ^+	−0.50	0.14	0.991
Benzenethiyl	Ethylbenzenes	Benzenethiol	5	σ	−0.82	0.59	0.934
Benzenethiyl	Ethylbenzenes	Benzenethiol	5	σ^+	−0.62	0.12	0.990

[a] The substituent constants were taken from R. D. Gilliam, "Introduction to Physical Organic Chemistry", Addison-Wesley, Reading, Mass., 1970. [b] Determined by the standard linear regression techniques. [c] Confidence limit given by (standard deviation of the slope)(t-test value at the 95% confidence level). See G. W. Snedecor, "Statistical Methods", 4th ed, Iowa State College Press, Ames, Iowa, 1946, pp 153 and 549; W. H. Davis, Jr., and W. A. Pryor, *J. Chem. Educ.*, **53,** 285 (1976).

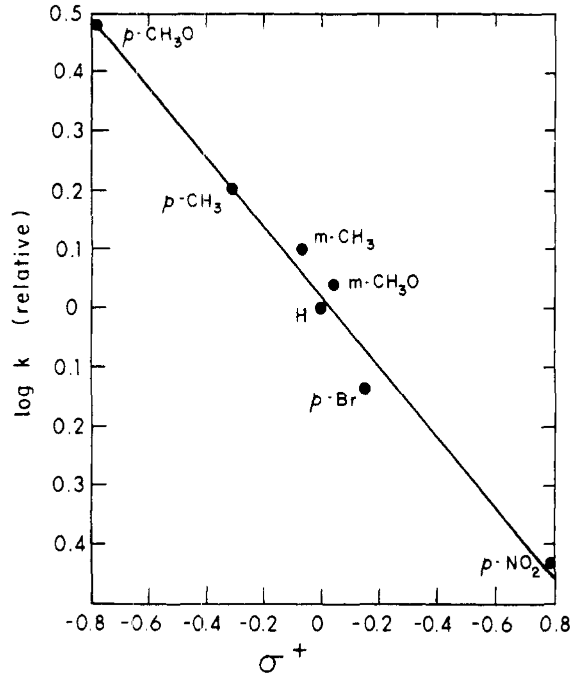


Figure 2. Hammett–Brown correlation for hydrogen abstraction from ethylbenzenes by the cyclohexanethiyl radical.

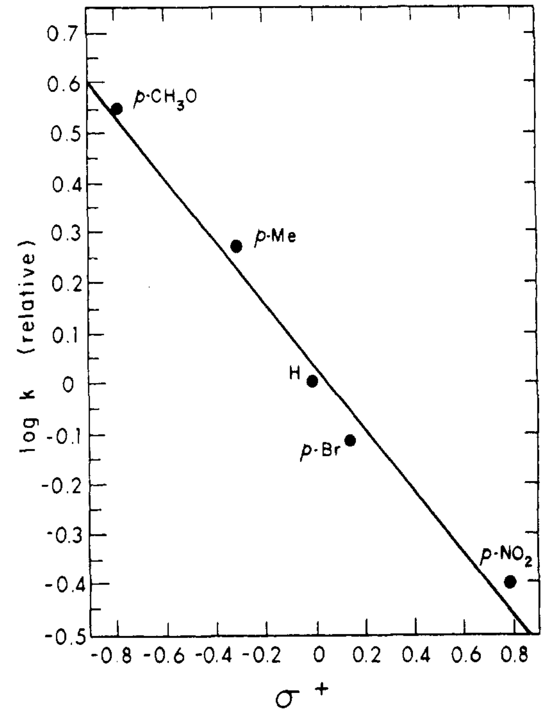
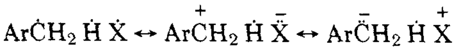


Figure 3. Hammett–Brown correlation for hydrogen abstraction from ethylbenzenes by the benzenethiyl radical.

Table V. The σ^+ parameters give a better correlation of the data in all cases except for hydrogen abstraction from toluenes by the cyclohexanethiyl radical. There, σ parameters give a markedly better fit; however, only four points could be determined in this series because of the low reactivity of the toluenes, and it is doubtful if the distinction between σ and σ^+ is statistically significant. As expected, these ρ values imply electrophilic character for both thiyl radicals.[24] The absolute values of ρ decrease as the hydrogen atom donor changes from toluene to ethylbenzene to cumene for abstraction by the cyclohexanethiyl radical. This is a trend also observed for bromine atoms.[25]

Similarity of ρ Values for Hydrogen Abstraction by the Two Thiyl Radicals. It is remarkable that the ρ values for hydrogen abstraction from ethylbenzene by the two thiyl radicals are, within experimental error, the same (see Table VI). The benzenethiyl radical has a substantially greater electron affinity than does the cyclohexanethiyl radical. Thus, according to the usual polar effects arguments,[4b,14,26] the transition state for hydrogen abstraction by the benzenethiyl radical should contain a larger contribution from the charge-separated form **2.** This should, in turn, lead to a more negative ρ.[26-28] Furthermore, abstraction by the benzenethiyl radical is 10 kcal/mol less exothermic than is abstraction by cyclohexanethiyl radical, and this also would lead one to expect a more negative ρ for the former reaction.[28,29]



$$\mathrm{Ar\dot{C}H_2\ H\ \dot{X}} \leftrightarrow \overset{+}{\mathrm{ArCH_2}}\ \mathrm{\dot{H}}\ \overset{-}{\mathrm{\dot{X}}} \leftrightarrow \mathrm{Ar\overset{-}{C}H_2\ \dot{H}\ \overset{+}{X}}$$

1 2 3

The results, however, show that the ρ values are the same, in spite of the differences in the electron affinities and heats of reaction of the two thiyl radicals. These are three possibilities that can account for this unexpected result.

(1) The experimentally determined ρ values may be in error. This does not seem likely. Both ρ values were determined by identical experimental procedures, and, as described in the Appendix, control experiments demonstrate the trustworthiness of the method.

(2) Another possibility is that both the electron affinities of the two thiyl radicals and the bond dissociation energies of the corresponding thiols are actually more nearly the same than the literature indicates. This is a rather stringent requirement, since if *either* the electron affinities or the BDE values are different, then a more negative ρ value for hydrogen abstraction by benzenethiyl radical would be expected.[26-28] However, it is not likely that either the electron affinities

Table VI. Thermochemical, Polar, and Kinetic Data on Three Radicals

	Radical, X·		
	$C_6H_{11}S\cdot$	PhS·	Br·
$X\cdot + ArCH_3$, ρ	-1.9^a		-1.8^b
$X\cdot + ArC_2H_5$, ρ^+	-0.6^a	-0.6^a	$-0.68^{b,c}$
Electron affinity, eV	1.5^d	2.5^e	3.36^f
BDE (X–H), kcal/mol	92	82	87
ΔH, $X\cdot + ArCH_3$, kcal/mol	−7	3	−2
ΔH, $X\cdot + ArC_2H_5$, kcal/mol	−10	0	−5
k_H/k_D using EtPh-d_{10}	8	8	
k_H/k_D using MePh-d_1			4.6^g
Polarizability^h	8.1	8.4	8.6

[a] This work. [b] W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Am. Chem. Soc.*, **95**, 6993 (1973); the value is extremely solvent dependent. [c] Recalculation of data of R. L. Huang and K. H. Lee, *J. Chem. Soc. C*, 935 (1966). [d] *n*-BuS·, ref 20b. [e] Upper limit, ref 20c. [f] Reference 19. [g] Value found in the solution phase by K. R. Wiberg and L. H. Slaugh, *J. Am. Chem. Soc.*, **80**, 3033 (1958). Tanner et al.[11b] suggest that this solution phase value may be low due to cage return. However, this value is comparable to the other solution phase values shown. [h] Reference 35.

or the BDE values are the same for both cyclohexanethiyl and benzenethiyl radicals. First, while the electron affinities are reported to differ by 1 eV or less, it is doubtful that they are identical.[20] Second, the BDE values of cyclohexanethiol and benzenethiol would not be expected to be identical. When we first discussed these data,[30] the BDE values for RS–H and PhS–H were reported to be 88 and 75 kcal/mol. At that time we proposed that[30] the similar selectivities we observed for the RS· and PhS· radicals "... suggests that the BDE's of the S–H bonds in cyclohexanethiol and benzenethiol do not differ by as much as is generally believed". Recently, Benson[31] has calculated these BDE to be 92 and 82 kcal/mol, respectively. Evidence can be cited which suggests that the actual BDE values for RSH and PhSH may be even more similar than Benson's new values indicate;[32–34] however, it is unlikely that they are sufficiently similar to rationalize the identical ρ values observed for the two thiyl radicals.

(3) The final possibility, and the one we favor, is that some as yet unidentified factor makes a significant contribution to the magnitude of ρ. Table VI includes data for not only the two thiyl radicals but also for bromine atoms. The ρ values for hydrogen abstraction from ethylbenzene by all three of these radicals are, essentially, the same. However, the electron affinities vary from 1.5 to 3.4 eV, while the heats of reaction range over 10 kcal/mol. Clearly, electron affinity and BDE arguments cannot be used here to rationalize the observed ρ values. However, it is interesting to note that there is one property of the attacking radical which is the same in all three cases. That property is the *polarizability* of that atom to which the bond with hydrogen will be formed.[35] Just as it is an important factor contributing to a species' nucleophilicity,[36] polarizability may also be significant in determining the electrophilicity of a radical in hydrogen abstractions.

Note Added in Proof: In an article just published, R. H. Krech and D. L. McFadden (*J. Am. Chem. Soc.*, **99**, 8402 (1977)) show that the activation energies for hydrogen abstraction reactions in a homologous series of exothermic reactions are proportional to the inverse of the polarizabilities of the hydrogen donor and the attacking atom. In this connection, it also is interesting that the absolute rate constant for the reaction of *tert*-butoxy radicals with cumene is reported to be 9×10^5 M^{-1} s^{-1} at 25 °C by R. D. Small, Jr., and J. C. Scaiano (private communication; submitted for publication in *J. Am. Chem. Soc.*). This value is quite similar to the rate constant for the reation of $C_6H_{11}S\cdot$ with cumene at 80 °C, approximatly 6×10^6 M^{-1} s^{-1} given in Table II and the discussion here. The heats of these two reactions are −25 and −13 kcal/mol, respectively.

Acknowledgments. This research was partially supported by grants from the National Institutes of Health and the National Science Foundation to W.A.P. We also wish to thank the Consejo Nacional de Ciencia y Tecnologia (Mexico) for a scholarship for G. Gojon and Dr. William H. Davis, Jr., for helpful discussion.

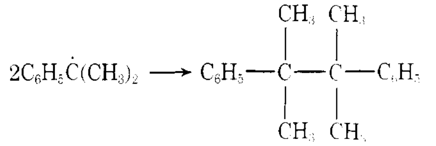
Appendix

Effect of Isolation Procedure on QH Activity. A sample of tritium-labeled triphenylmethane (6.8×10^8 dpm/mol, recovered from kinetic runs) was subjected to the normal workup procedure; no decrease in the activity was observed. Therefore, exchange between the benzylic hydrogens in the substrate and those of water (or other molecules) upon workup can be excluded, even for the more reactive substrates studied. Quantitative collection (trapping) was demonstrated for every liquid substrate studied by control experiments.[10] The assumptions that [RSH] ≫ [RST], low conversions, and the low extent of labeling of QH were met. (About one thiol molecule in 10^5 contained tritium.)

Most of the critical assumptions made in deriving eq 11 and 17 amount to the neglect of specific reactions. Such "wrong" reactions were ruled out on the basis of control experiments that are discussed in the paragraphs below.

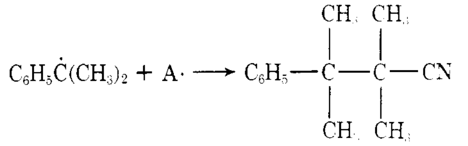
Controls on Q· + X·, Reactions 18–21. If a Q· radical participates in termination reactions instead of reverting to (labeled) donor, the abstraction reaction that led to the Q· radical would not be detected, and the activity level in the recovered QH would be spuriously low. Cumene was chosen as a model substrate to study possible Q· termination reactions.

Participation of cumyl radicals in termination reactions[6] (eq 18–21) was ruled out by detailed product studies in cyclohexanethiol solvent (Table I) using GLC of reaction mixtures similar to those in the competitive method (eq 3–7) but containing cumene (0.25–0.5 M) as the only hydrogen donor. (In eq 18–21, A· is a 2-cyano-2-propyl radical and X· is any radical in the system.) Equation 22 depicts the most probable

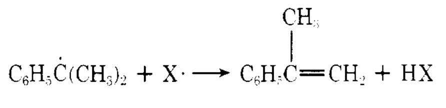


$$2C_6H_5\dot{C}(CH_3)_2 \longrightarrow C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5 \qquad (18)$$

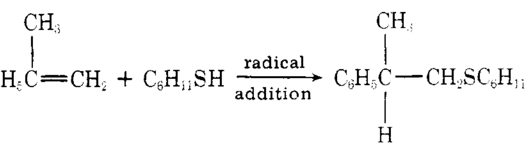
$$C_6H_5\dot{C}(CH_3)_2 + C_6H_{11}S\cdot \longrightarrow \underset{\mathbf{1}}{C_6H_5C(CH_3)_2SC_6H_{11}} \qquad (19)$$



$$C_6H_5\dot{C}(CH_3)_2 + A\cdot \longrightarrow C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CN \qquad (20)$$



$$C_6H_5\dot{C}(CH_3)_2 + X\cdot \longrightarrow C_6H_5\overset{CH_3}{C}{=}CH_2 + HX \qquad (21)$$



$$\overset{CH_3}{C_6H_5C}{=}CH_2 + C_6H_{11}SH \xrightarrow[\text{addition}]{\text{radical}} C_6H_5\overset{CH_3}{\underset{H}{C}}-CH_2SC_6H_{11} \qquad (22)$$

5

fate[6] of the α-methylstyrene formed in reaction 21. The amounts of bicumyl and of sulfides **4** and **5** produced in these control reaction mixtures could account for less than 1% of the cumyl radicals generated. Table I shows that the yield of AH (isobutyronitrile) (for 0.5 M cumeme) is roughly twice that of dicyclohexyl disulfide, indicating that dimerization of the thiyl radicals (eq 23) is the most important termination reaction occurring in free solution in systems containing up to 0.5 M cumene.

$$2C_6H_{11}S\cdot \rightarrow C_6H_{11}S\text{–}SC_6H_{11} \tag{23}$$

As cumene concentration increases, the observed trends in the yields of bicumyl and **5** are consistent with expectations based on our kinetic analysis; specifically, a proportionality between the steady-state concentration of $Q\cdot$ and the concentration of QH is predicted.[10] Thus, neither bicumyl nor sulfide **5** is found in reaction mixtures up to 0.5 M in cumene (runs 1–4, Table I), but they both form in substantial amounts when 2.5 M cumene is used (run 5). Therefore, as QH and $Q\cdot$ concentrations increase, there is an enhancement in the rates of termination reactions in which $Q\cdot$ participates and in the yields of the corresponding termination products. At the highest cumene concentration (run 5) the ratio of molar yields of disulfide to isobutyronitrile (AH) falls to 0.31, a value which is consistent with the observation of termination reactions other than disulfide formation. Since 19 out of 25 substrates investigated are less reactive than cumene, they are expected to give rise to lower steady-state concentrations of $Q\cdot$ and less termination involving $Q\cdot$ radicals.

Controls on $Q°\cdot$ + QH, Reaction 24. It is possible that radicals other than $RS\cdot$ might abstract hydrogen from QH. In competitive runs (eq 3–7), for instance, reaction 24 could take place. Reaction 24 is likely to introduce complications by quenching the radicals ($Q°\cdot$) from the less reactive donor, without labeling them, and simultaneously generating $Q\cdot$ radicals which become labeled and counted, leading to spuriously high $A_{QH}/A_{Q°H}$ ratios.

$$Q°\cdot + QH \xrightarrow{k_{24}} Q°H + Q\cdot \tag{24}$$

The self-consistency of relative rates obtained within the framework of the competitive method, eq 3–7, can be tested in the following manner. The relative reactivities of substrates A and B are determined by a direct competition, and the results are compared with the outcome of a calculation based on the results of two actual competitions, one between A and C (a third substrate) and another between B and C (eq 25). Equation 25 can be justified only if rate constant ratios are proportional to the ratio of the rate constants if reaction 24 is included in the kinetic scheme. The excellent agreement observed between directly and indirectly obtained rate constant ratios[10] suggests that reaction 24 must not occur.

$$\frac{(k)_A}{(k)_B} = \frac{(k)_A}{(k)_C}\frac{(k)_C}{(k)_B} \tag{25}$$

We also studied the effect of variations in the experimental parameters on the measured relative reactivities. The competition between ethylbenzene and cumene toward the cyclohexanethiyl radical was chosen as a model; reaction times were varied 4.3-fold, extents of reaction by 2.4-fold, concentration of combined donors sevenfold, and ratio of concentrations of donors 20-fold. None of these variations affected the measured relative reactivities.[10] Use of *tert*-butyl cyclohexaneperoxycarboxylate in place of AIBN also failed to affect the relative k_H values.[10] The rate of reaction 24 is modified by the above variations, but the activity ratios and, consequently, the ratio of rate constants for cumene and ethylbenzene remain constant, suggesting that reaction 24 is not kinetically significant.

Controls on $C_6H_{11}\cdot$ + QH, Reaction 26. The "reference reaction" in the second method is desulfuration of cyclohexanethiyl radicals by TPP, eq 12;[12] this yields cyclohexyl radicals that might abstract hydrogen from the donor (QH) present in the sample (eq 26). Occurrence of reaction 26 would lead to spuriously high reactivities. As stated above, use of *tert*-butyl cyclohexaneperoxycarboxylate instead of AIBN as the initiator did not affect the measured relative reactivities; this perester yields *tert*-butoxy and cyclohexyl radicals, and if either of these radicals attacked the substrates in kinetically significant amounts, the values of k_H would have been affected. The linearity observed in plots[10] of A_{QH} [TPP] vs. [C_6H_{12}] also argues against the occurrence of reaction 26. In addition, inclusion of reaction 26 in the kinetic scheme would not allow elimination of the terms involving concentrations of reactive intermediates, and the final equation would no longer lead to linear plots. Finally, the excellent agreement of the results obtained by both kinetic methods[8] suggests that reaction 26 does not interfere when the second method is used.

$$C_6H_{11}\cdot + QH \rightarrow C_6H_{12} + Q\cdot \tag{26}$$

Controls on $A\cdot$ + QH, Reaction 27. If 2-cyano-2-propyl radicals ($A\cdot$) from AIBN abstract hydrogen from the substrate(s), the observed selectivities would be characteristic of $A\cdot$ radicals and not of $RS\cdot$ radicals. However, since the same reactivity ratios were obtained when either *tert*-butyl peroxycyclohexanecarboxylate or AIBN initiation was used, such ratios reflect abstraction by some radical other than $A\cdot$.

$$A\cdot + QH \rightarrow AH + Q\cdot \tag{27}$$

Controls on Miscellaneous Reactions. It is conceivable that the nucleus of the aromatic substrates might become labeled. However, oxidative degradation of labeled ethylbenzene (recovered from kinetic runs) yields benzoic acid without residual activity. It is also possible to envision labeling and/or cyclohexane formation taking place via ionic or other unidentified pathways. The absence of labeling and cyclohexane in reaction samples from kinetic runs in which no initiator had been used excludes these complications.

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(33) Hydrogen abstraction by hydrogen atoms from *tert*-butyl mercaptan and benzenethiol occurs at the same rates within experimental error. See W. A. Pryor and J. P. Stanley, *J. Am. Chem. Soc.*, **93,** 1412 (1971).

(34) An argument that the BDE for RS–H and PhS–H is the same could be based on the fact that the isotope effects are the same for both thiyl radicals. (See Table VI.) However, this is not convincing. First, the plot of isotope effects vs. BDE is relatively flat at its top;[9a] since both of these isotope effects are about 8 and are near the maximum values, they occur in a region where the isotope effect is not sensitive to small changes in the BDE.[9a] Second, it is possible that the RS· reaction has an early transition state and the PhS· a late transition state, such that, by coincidence, both isotope effects are the same.[9a]

(35) (a) The measure of polarizability used here is the molar refractivity which is proportional to the atomic (molecular) polarizability.[35b] The molar refractivity is a group additive property and is, thus, readily determined.[35c] (b) G. W. Castellan, "Physical Chemistry", Addison-Wesley, Reading, Mass., 1964, pp 470 ff. (c) R. J. W. Le Fevre, "Advances in Physical Organic Chemistry", Vol. 3, V. Gold, Ed., Academic Press, New York, N.Y., 1965, pp 1–90.

(36) It is believed that the more polarizable atoms are better able to reduce electron density in the vicinity of the nascent bond, thereby reducing Pauli repulsions. See the discussion in J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84,** 16 (1962).

Stable Free Radicals. 7. 1-Alkyl-4-carbomethoxypyridinyls

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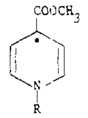
Received October 11, 1977

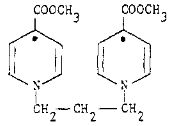
The synthesis of the 1-*tert*-butyl-4-carbomethoxypyridinyl radical is described and its properties are compared with the corresponding 1-methyl, 1-ethyl, and 1-isopropyl radicals. Although the *tert*-butyl radical appears to be the most stable in pure form and less susceptible to π-mer formation, its chemical reactivity toward bromochloromethane is very similar to that of the other 1-alkyl radicals. The nature of the products of reaction of 1-isopropyl-4-carbomethoxypyridinyl with bromochloromethane has been elucidated.

Stable pyridinyl radicals[2,4] (1) were first isolated in 1963[5] and have since proven useful for mechanistic studies.[6,7] Pyridinyl diradicals (e.g., 2) were also prepared and examined.[8,9]



1

R = $CH_3, CH_3CH_2,$
$(CH_3)_2CH, (CH_3)_3C$



2

The formation of π-mers from pyridinyl monoradicals (intermolecular)[10] and from diradicals[9,11] (intramolecular) made necessary an understanding of the effect of *N*-alkyl substitution on the properties of pyridinyl monoradicals. Our more recent discovery of pyridinyl radical complexation with bis(pyridinium) ions[12] accentuated the need. Although the 1-ethyl radical has been described previously,[13] only few data have been noted for the 1-methyl and 1-isopropyl radicals.[10] We have now been able to complete the series with the 1-*tert*-butyl radical and shall describe in this article the preparation and certain properties of the simplest 1-alkyl-4-carbomethoxypyridinyl radicals (1).

Results

Synthesis of Salts. Methyl isonicotinate readily reacts with methyl, ethyl, and isopropyl iodides to form the desired salts

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