sec^{-1} were recorded. After the irradiation the degree of reaction was determined either by quantitative ultraviolet spectroscopy, nmr spectroscopy, or vapor phase chromatography (6 ft × 0.25 in. 10% SE-30 methylsilicone gum rubber on Diatoports at 243°). The conversions in the aziridine series were run to 15% or less. The mass balance in these runs was generally better than 95%.

Phosphorescence Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on a X–Y plotter. Samples having short radiative lifetimes (<100 msec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (T_0).

Electron Paramagnetic Resonance Spectra. Electron paramagnetic resonance spectra were measured using a Varian X-band (Model *V*-4502) spectrometer having a modulation frequency of 100 KHz. Spectra were recorded with the rf magnetic field perpendicular to the static field. The sample solutions were sealed in 4-mm o.d. quartz tubes after degassing on a vacuum line. The sample was irradiated in a slotted face Varian *V*-4531 cavity. Light from a 450-W (Hanovia, type L) mercury arc lamp was focused through a quartz optical system. The sample was cooled by a flow of cold nitrogen gas which was passed through a heat-exchange coil submerged in liquid nitrogen.

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Reactions of the Hydrogen Atom in Solution. III. The Photolysis of Thiols. Studies of Tritium-Labeled Thiols[1-3]

William A. Pryor* and Michael G. Griffith

Contribution from the Department of Chemistry,
Louisiana State University, Baton Rouge, Louisiana 70803.
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Abstract: Propanethiol, tritiated at the S–H bond, has been photolyzed in the presence of various organic hydrogen donors (QH). Tritium becomes incorporated both into the thiol side chain and into QH. A relation is derived between the rate of formation of labeled QH (*i.e.*, d(QT)/d*t*) and the rate constant k_H for the reaction $H\cdot + QH \rightarrow H_2 + Q\cdot$. In order to avoid errors produced by changes in light flux from run to run, the rate of formation of QT is measured relative to the rate of formation of side-chain labeled thiol. This method gives correct values of k_H for alkanes where the Q–H bond being broken is much stronger than the RS–H bond. Compounds such as toluene which contain weak C–H bonds give spuriously high values of k_H. For these compounds the thiyl radical, and possibly also the carbon radical resulting from hydrogen abstraction from the side chain of the thiol, are able to convert QH to $Q\cdot$. The isotope effect k_T/k_H for the reaction of $Q\cdot$ with RSH or RST must be known before values of k_H can be calculated; this isotope effect can be evaluated directly in independent measurements and data are presented for several $Q\cdot$ radicals.

The nature and reactivity of the hydrogen atom is inherently of great interest. Relative rate constants for the reaction of hydrogen atoms with a range of water soluble substances have been obtained from the radiolysis of aqueous solutions, and these relative rate constants can be put on an absolute basis using pulse radiolysis techniques.[4] The hydrogen atom has also been studied in the gas phase.[5] It is desirable to obtain rate constants for the reaction of hydrogen atoms with organic hydrogen donors in organic solutions. In other papers in this series, we have reported methods for obtaining these data.[2] In this paper, we report our earliest attempt[3] to discover a kinetic system which would lead to values of k_H, the rate constant for reaction I. The method we report here is the photolysis of

$$H\cdot + QH \xrightarrow{k_H} H_2 + Q\cdot \qquad \text{(I)}$$

mixtures of an aliphatic thiol which is tritiated at the S–H bond and an organic hydrogen donor QH. Tritium becomes incorporated into the donor, and the rate of formation of QT can be related to the rate constant for reaction I. As we have shown elsewhere,[2a-c] this method gives reliable values of k_H for cases where the Q–H bond is much stronger than the RS–H bond, as, for example, is true in the alkanes. This system gives spurious results, however, for QH compounds with weak bonds; in these cases the thiyl radical RS· also is

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(1) Reactions of Radicals. XXXV. We wish to acknowledge the support of the USPHS under Grant GM-11908 from the National Institutes of Health. M. G. Griffith was a NASA Predoctoral Trainee from Sept 1963 to Aug 1966 and a research associate on this NIH grant from 1966 to 1968.

(2) Earlier papers in this series are (a) I: W. A. Pryor, J. P. Stanley, and M. G. Griffith, *Science*, **168**, 181 (1970); (b) II: W. A. Pryor and J. P. Stanley, *Intrasci. Chem. Rept.* **4**, 99 (1970); (c) IV: W. A. Pryor and J. P. Stanley, *J. Amer. Chem. Soc.*, **93**, 1412 (1971); (d) V: W. A. Pryor and R. W. Henderson, *ibid.*, **92**, 7234 (1970).

(3) Abstracted in part from the Ph.D. Dissertation of M. G. Griffith, Louisiana State University, Jan 1968.

(4) (a) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand, New York, N. Y., 1961; (b) M. Ebert, J. P. Keene, and A. J. Swallow, Ed., "Pulse Radiolysis," Academic Press, New York, N. Y., 1965; (c) G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1738 (1964); (d) M. Anbar and D. Meyerstein, *ibid.*, **68**, 3184 (1964); (e) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc.*, 572 (1966); (f) J. Rabani, *J. Phys. Chem.*, 66, 361 (1962).

(5) (a) B. A. Thrush, *Progr. Reaction Kinetics*, 3, 63 (1965); (b) K. Yang, *J. Phys. Chem.*, 67, 562 (1963); (c) K. J. Laidler, "Theories of Chemical Reaction Rates," McGraw-Hill, New York, N. Y., 1969.

able to abstract hydrogen from QH. Nevertheless, this system is of interest from the viewpoint of radiation protection and radiobiology,[6,7] since in radiation protection studies both hydrogen atoms and thiyl radicals are present and can cause damage in the same way as they do in this system.

Experimental Section

Materials used were all reagent or spectro grade and were purified as necessary. Runs were done in sealed quartz ampoules connected to a Pyrex upper end by a graded seal. Samples were prepared by weighing out QH and thiol into 3-ml volumetric flasks and transferring to the ampoules which were then degassed and sealed under vacuum. The tubes were inserted into a Vycor 7913 condenser which was standing vertically and centered in a Rayonet Srinivasan-Griffin photochemical reactor. The 3000-Å lamps were used. Water held at 40° ± 0.05° was circulated through the condenser for the duration of the irradiation, which was always 12 hr.

The ampoules were cooled and opened, and a known amount of QH was added as a diluent. The thiol and QH were separated and analyzed in various ways depending upon the nature of QH. The hydrocarbons and *p*-dioxane were separated from the thiol by distillation.[8] Traces of the highly radioactive thiol were efficiently removed by washing with dilute aqueous base, and the substrates were redistilled to constant activity (twice was usually sufficient). The *p*-dioxane was washed with small amount of 5 *N* aqueous KOH to reduce its solubility in the aqueous phase.

Activity was incorporated into both the ring and the side chain of the aromatic substrates. The activity in the side chain was determined by counting the unmodified substrate, then oxidizing (or modifying) the side chain to eliminate tritium from that site, and recounting. The difference gives the activity at the side chain position and was used in eq 11. Oxidation of toluene and ethylbenzene to benzoic acid was accomplished by refluxing with basic $KMnO_4$.[9a] This was not successful with cumene (nor was acidic $K_2Cr_2O_7$ or $Na_2Cr_2O_7$), so another approach was used to separate ring and side-chain activity. Cumene was brominated in CCl_4, and the resulting 2-bromo-2-phenylpropane was solvolyzed in methanol to methyl 2-phenyl-2-propyl ether. It was assumed in all three alkylbenzenes that the only activity of significant magnitude in the side chain was at the benzylic hydrogens.

The runs involving alcohols as substrates were preheated at 40° for several hours before irradiation. It was assumed that tritium became equilibrated between alcohol and thiol, and a corrected value of A_{th}^0 was used in eq 11 and 13.

The alcohols were counted as their phenylurethan derivatives.[9b] Controls showed that the 1-propanethiol did not interfere with this reaction. The urethan incorporates the hydroxyl hydrogen and this tritium is not a part of the alkyl group of the alcohol. Therefore, these derivatives were recrystallized from ethanol–water mixtures to constant activity; this allowed the unwanted tritium on nitrogen to exchange with the solvents and thus be removed from the derivative. With 2-propanol, three recrystallizations were sufficient but five or six were required for the other two alcohols. Controls verified that derivatives prepared from alcohols tritiated only at oxygen could be reduced to background levels after the appropriate number of recrystallizations. Melting points of the urethans agreed with those reported in the literature.

Activity in the alkyl group of the thiol was determined by preparing the *S*-propyl ester of diphenylcarbamic acid.[10] Thiol from a distillation (or simply part of the contents of an ampoule containing thiol) was added to a solution of sodium ethoxide. A hot solution of diphenylcarbamoyl chloride in ethanol was poured in, and the solution was filtered and cooled. The derivative was recrystallized from ethanol–water to give *S*-propyl diphenylthiocarbamate with mp 52–53°.

Tritium activity in the various samples was measured with a Packard Tri-Carb liquid scintillation spectrometer, Model 3365. The counting efficiency of each sample was determined by comparison with a set of quenched standards obtained from Packard. Each sample was counted for a period sufficient to reduce the random error to 2% or less (*i.e.*, at least 10,000 counts), with the exception of the phenylurethans of methanol. These derivatives were of such low activity that a small number of counts are collected.

Results

A preliminary study of the photolysis of thiols tritiated at the S–H bond revealed that tritium becomes incorporated both into the side chain of the thiol and also into any added substrate which has abstractable hydrogens. After a number of screening experiments, we elected to study in detail the photolysis of propanethiol using the 3000-Å Rayonet lamps and 40°. Reactions I and 1–8a are responsible for the labeling of the thiol and the organic hydrogen donor QH, where (HQH)· or (TQH)· is any addition complex which QH may form with hydrogen (or tritium) atoms, Pr*SH is side-chain labeled thiol, and I_7 and I_8 are the appropriate factors to allow for the isotope effects on reactions 7 and 8 (see Discussion). Runs were limited so that no more than 1% of the activity became incorporated into QH, and under these circumstances the reversal of eq 8a is kinetically unimportant.

rate constant

$$\mathrm{PrSH} \xrightarrow{h\nu} \mathrm{PrS}\cdot + \mathrm{H}\cdot \qquad k_d \tag{1}$$

$$\mathrm{H}\cdot + \mathrm{PrSH} \longrightarrow \mathrm{PrS}\cdot + \mathrm{H_2} \qquad k_2 \tag{2}$$

$$\mathrm{H}\cdot + \mathrm{PrSH} \longrightarrow \mathrm{Et\dot{C}HSH} + \mathrm{H_2} \qquad k_3 \tag{3}$$

$$\mathrm{H}\cdot + \mathrm{QH} \longrightarrow \mathrm{Q}\cdot + \mathrm{H_2} \qquad k_H \tag{4}$$

$$\mathrm{H}\cdot(\mathrm{T}\cdot) + \mathrm{QH} \longrightarrow (\mathrm{HQH})\cdot \text{ or } (\mathrm{TQH})\cdot \qquad k_{ad} \tag{5}$$

$$\mathrm{PrSH(T)} + \mathrm{PrS}\cdot \longrightarrow \text{no change} \tag{6}$$

$$\mathrm{PrSH} + \mathrm{Et\dot{C}HSH} \longrightarrow \mathrm{PrS}\cdot + \mathrm{PrSH} \qquad k_7 \tag{7}$$

$$\mathrm{PrST} + \mathrm{Et\dot{C}HSH} \longrightarrow \mathrm{PrS}\cdot + \mathrm{Pr^*SH} \qquad k_7I_7 \tag{7a}$$

$$\mathrm{PrSH} + \mathrm{Q}\cdot \longrightarrow \mathrm{PrS}\cdot + \mathrm{QH} \qquad k_8 \tag{8}$$

$$\mathrm{PrST} + \mathrm{Q}\cdot \longrightarrow \mathrm{PrS}\cdot + \mathrm{QT} \qquad k_8I_8 \tag{8a}$$

The thiol is assumed to photolyze primarily by S–H bond scission[2b,11] to form a thiyl radical and a hydrogen atom (eq 1). The hydrogen atom then abstracts hydrogen from the S–H bond of the thiol (eq 2), from the propyl group of the thiol (eq 3), or from the substrate QH (eq 4). All of these radicals are then assumed mainly to be scavenged by thiol. The main scavenging species of course is PrSH, but reactions 7a and 8a illustrate the scavenging of radicals by the tritiated thiol, PrST, since it is in these steps that the alkyl side chain of the thiol and the substrate QH become labeled. Reaction 5 is included because some of the substrates we have studied may add hydrogen atoms (toluene, for example). The nature and fate of the addition complex (HQH)· or (TQH)· are assumed not to affect the analysis of the hydrogen abstraction reactions given here.[12]

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(6) A. P. Casarett, "Radiation Biology," Prentice-Hall, Englewood Cliffs, N. J., 1968.

(7) Z. M. Bacq and P. Alexander, "Fundamentals of Radiobiology," Pergamon Press, New York, N. Y., 1966.

(8) In our more recent work we use a gas flow counter coupled to gas chromatography for this.

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, London, 1956, (a) p 250; (b) pp 222, 280.

(10) R. G. Hiskey, F. I. Carroll, R. F. Smith, and R. T. Corbett, *J. Org. Chem.*, **26**, 4756 (1961).

(11) W. E. Haines, G. L. Cook, and J. S. Ball, *J. Amer. Chem. Soc.*, **78**, 5213 (1956); T. Inaba and B. deB. Darwent, *J. Phys. Chem.*, **64**, 1431 (1960); D. A. Stiles, W. J. R. Tyerman, O. P. Strausz, and H. E. Ganning, *Can. J. Chem.*, **44**, 2149 (1966); R. P. Steer, B. L. Kalra, and A. R. Knight, *J. Phys. Chem.*, **71**, 784 (1967).

(12) However, when the substrate can also add hydrogen atoms, the activity must be measured in such a way as to count only that activity which has been incorporated as a result of reaction 4. For example, for toluene the total activity and the activity of the benzoic acid resulting from oxidation are determined.

The rate of production of labeled substrate, d(QT)/d*t*, is related to R_8, the total rate of reaction of Q· with PrSH, by eq 9, where $A_{\mathrm{th}}{}^0$ is the initial molar specific

$$\frac{\mathrm{d(QT)}}{\mathrm{d}t} = \frac{\mathrm{d(QH)(PrST)}}{\mathrm{d}t\mathrm{(PrSH)}}\left(\frac{k_{\mathrm{T}}}{k_{\mathrm{H}}}\right)_8 = R_8A_{\mathrm{th}}{}^0I_8 \qquad (9)$$

activity of the thiol (which is unchanged in any run because of the low conversions studied), and I_8 is the isotope effect,[13] $k_{\mathrm{T}}/k_{\mathrm{H}}$, on reaction 8. Using the steady-state approximations for Q· and H·, we obtain eq 10,

$$\frac{\mathrm{d(QT)}}{\mathrm{d}t} = A_{\mathrm{th}}{}^0I_8k_{\mathrm{H}}\mathrm{(QH)(H\cdot)} = \frac{A_{\mathrm{th}}{}^0I_8k_{\mathrm{H}}k_{\mathrm{d}}\mathrm{(QH)_0(PrSH)_0}}{(k_2 + k_3)\mathrm{(PrSH)_0} + (k_{\mathrm{H}} + k_{\mathrm{ad}})\mathrm{(QH)_0}} \qquad (10)$$

where the subscript zeros indicate initial concentrations. Integration of eq 10 assuming low conversions and unchanging concentrations followed by inversion and rearrangement gives eq 11, where *t* is the duration of the

$$\frac{(t)\mathrm{(PrSH)_0/(QH)_0}}{A_{\mathrm{QH}}/A_{\mathrm{th}}{}^0} = \frac{(k_{\mathrm{H}} + k_{\mathrm{ad}})/k_{\mathrm{d}}}{k_{\mathrm{H}}I_8} + \frac{(k_2 + k_3)/k_{\mathrm{d}}\mathrm{(PrSH)_0}}{k_{\mathrm{H}}I_8\mathrm{(QH)_0}} \qquad (11)$$

photolysis in seconds and A_{QH} is the molar specific activity of QH produced in the experiment. The left side of eq 11 contains quantities which can be measured, and $(k_2 + k_3)/k_{\mathrm{d}}$ will be a constant for any series of runs providing the light intensity and geometry of the photolysis are unchanged. Therefore, a graph of the left side of eq 11 *vs.* $\mathrm{(PrSH)_0/(QH)_0}$ should be a straight line with slope inversely proportional to $k_{\mathrm{H}}I_8$.

We have studied a number of substrates, and all give straight lines when the data are plotted according to eq 11. Usually the ratio of thiol to QH concentration is varied over approximately a tenfold range.[3]

If all the runs could be done under conditions of constant light flux, plots of eq 11 could be used to obtain relative values of $k_{\mathrm{H}}I_8$. In practice, however, the light source will diminish in intensity with time. To allow for this and other factors which could affect the light flux, we have used a procedure in which the rate of incorporation of activity into the side chain of the thiol is used as an internal standard. The rate of formation of side-chain labeled thiol is given by

$$\frac{\mathrm{d(Pr^*SH)}}{\mathrm{d}t} = R_7A_{\mathrm{th}}{}^0I_7 = k_3I_7A_{\mathrm{th}}{}^0\mathrm{(PrSH)(H\cdot)} \qquad (12)$$

where R_7 is the total rate for the reaction of $\mathrm{Et\dot{C}HSH}$ with PrSH, I_7 is $k_{\mathrm{T}}/k_{\mathrm{H}}$ for eq 7, and the steady-state approximation in $\mathrm{Et\dot{C}HSH}$ is assumed. Use of the steady-state approximation in H· followed by integration, rearrangement, and inversion then gives eq 13,

$$\frac{(t)\mathrm{(PrSH)_0/(QH)_0}}{A_{\mathrm{alkyl}}/A_{\mathrm{th}}{}^0} = \frac{(k_{\mathrm{H}} + k_{\mathrm{ad}})/k_{\mathrm{d}}}{k_3I_7} + \frac{(k_2 + k_3)/k_{\mathrm{d}}\mathrm{(PrSH)_0}}{k_3I_7\mathrm{(QH)_0}} \qquad (13)$$

where A_{alkyl} is the molar specific activity of the alkyl-labeled thiol. A plot of eq 13 has a slope inversely proportional to k_3I_7, which are the analogous quantities to those obtained for QH from eq 11. The ratio of the slopes of eq 13 to eq 11 for a series of runs with a given QH then gives

$$\frac{\text{(slope of eq 13 for a QH-thiol series)}}{\text{(slope of eq 11 for the same series)}} = \frac{k_{\mathrm{H}}I_8}{k_3I_7} = k_{\mathrm{H,rel}}I_8 \qquad (14)$$

where $k_{\mathrm{H,rel}}$ is the rate constant for reaction 4 compared to k_3I_7 as a standard. Table I gives data obtained in this way for a range of substrates.[14]

Table I. Relative Rates of Hydrogen Abstraction by Hydrogen Atoms from Various Substrates at 40° Using 3000-Å Light

QH	n[a]	$k_{\mathrm{H}}I_8/k_3I_7$[b]	$k_{\mathrm{H,rel}}I_8$ (per H)[c]
Cyclohexane	12	0.94	0.078
Hexane	8	0.63	0.079
Dodecane	20	1.45	0.072
2,3-Dimethylbutane	2	1.18	0.59
Methanol[d,f]	3	0.26	0.086
p-Dioxane	8	0.91	0.11
Ethanol[d]	2	3.23	1.61
2-Propanol[d]	1	10.5	10.5
Toluene[e]	3	0.40	0.13
Ethylbenzene[e]	2	8.5	4.2
Cumene[e]	1	22.8	22.8
p-Xylene[e]	6	1.68	0.28
p-Toluonitrile[e]	3	0.34	0.11
m-Fluorotoluene[e]	3	0.48	0.16
Methyl *p*-toluate[e]	3	0.46	0.15

[a] Number of reactive hydrogens. [b] Calculated as in eq 14. [c] Previous column divided by *n*, the number of reactive hydrogens. Only benzylic hydrogens are considered reactive for toluenes and the reactivity of secondary and primary hydrogens is neglected relative to that of tertiary hydrogens in alkanes, etc. [d] Data corrected to allow for equilibration of tritium between OH of alcohol and the SH of the thiol. See Experimental Section. [e] Data corrected so that only activity in the side chain is used; rate constants are therefore for abstraction of benzylic hydrogens. [f] These numbers are only approximate since very little activity is incorporated into the methanol.

Discussion

This system for measuring the rates of hydrogen atoms has a very serious drawback: any radical which abstracts a hydrogen from QH to produce the Q· radical can lead to the production of QT, the product which is observed. It was assumed in the derivation of eq 11–14 that the hydrogen atom is the only radical which abstracts from QH, and this assumption must be examined in more detail. If either the thiyl radical, RS·, or the carbon-centered radical, $\mathrm{Et\dot{C}HSH}$, abstracted hydrogen from QH, then spuriously large yields of QT would be produced. The rate constant k_{H} for abstraction from QH by H atoms is certainly much larger than is k_{s}, the rate constant for the reaction in which the sulfur of a thiyl radical attacks QH.

$$\mathrm{QH + RS\cdot \xrightarrow{k_s} Q\cdot + RSH} \qquad (15)$$

However, the thiyl radical is maintained at a much

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[13] The isotope effect appears in this form, rather than the inverse, since less activity is incorporated into QH than would have occurred if an isotope effect did not exist.

[14] D. Perner and R. H. Schuler [*J. Phys. Chem.*, **70**, 317 (1966)] have briefly described a system which may yield data analogous to those from our study.

higher steady state level in this system than is the hydrogen atom; this is because reaction 2 is a fast process which converts a large fraction of the hydrogen atoms to thiyl radicals. Thus, the larger concentration of thiyl radicals relative to H atoms could result in an appreciable amount of the abstraction being done by the thiyl radical. The rate constant k_c in which the carbon radical of the thiol attacks QH also is smaller than k_H.[2b] At this time it is not clear whether reaction

$$\mathrm{QH} + \mathrm{Et\dot{C}HSH} \xrightarrow{k_c} \mathrm{Q\cdot} + \mathrm{Et\overset{\overset{H}{|}}{C}HSH} \qquad (16)$$

16 is kinetically significant. However, the data presented in our other papers[2] demonstrate that reaction 15 is important for QH compounds which have bonds weaker than the RS–H bond. This largely destroys the usefulness of this system for measuring k_H values, since plots of eq 11 give straight lines even for those QH compounds where the thiyl radical does a significant amount of the abstraction from QH. This system, therefore, must be limited to studies of the reaction of the hydrogen atom with alkanes.

It is not surprising that reaction 15 competes with reaction 1 for QH compounds which have weak bonds.[15] The data of Table II show that the reaction of an aliphatic thiol with toluene, for example, is exothermic. The data in the table also show that thiophenol, which has a weaker S–H bond and produces a less reactive thiyl radical, reacts with toluene in an endothermic reaction. It is possible that the use of thiophenol in this system will allow values of k_H to be evaluated for QH compounds other than alkanes, and we are presently examining this possibility.[16]

Table II. Bond Strengths of Thiols and QH Donors and Calculated Heats of the Reaction $RS\cdot + QH \rightarrow RSH + Q\cdot$

Thiol	QH	Calcd ΔH[a]
Aliphatic, RSH[b]	Cyclohexane	+10
Aliphatic, RSH[b]	Toluene	−3
Aromatic, C_6H_5SH	Cyclohexane	+23
Aromatic, C_6H_5SH	Toluene	+10

[a] The following bond dissociation energies were used (kcal/mol): CH_3S–H, 88; PhS–H, 75; C_6H_{11}–H, 98; $PhCH_2$–H, 85. See J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [b] All simple aliphatic thiols have the same S–H bond dissociation energy; see H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

The data of Table II lead to the prediction that an aliphatic thiyl radical should abstract hydrogen rapidly from toluene and similar compounds but much less rapidly from alkanes. Walling was among the first to point this out, and some years ago he reported a study of the photolysis of isobutyl disulfide in QH donors which conclusively establishes this.[17] Table III shows some of these data.

Table III. Yields of Thiol Obtained from Photolysis of Isobutyl Disulfide in Various QH Hydrogen Donors[a]

QH	% conversion to thiol
Cumene	34
Isopropyl ether	7.8
sec-Butyl alcohol	6.5
Fluorene	6.0
Benzaldehyde	2.5
Diethyl malonate	1.5
Anisaldehyde	0.5

[a] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959); 35° and a low pressure mercury arc with output chiefly at 1849 and 2537 Å. The thiol also undergoes photolysis in this system; irradiation was continued until the thiol reached a steady concentration.

The Evaluation of I_8. Isotope Effects on the Reaction of Radicals with Thiols. Values of I_8 can be determined independently by generating radicals from a free-radical initiator in the presence of tritiated thiols. Table IV shows some of the data of this sort which we have accumulated. The values of k_H/k_T for the reaction of methyl and cyclohexyl radicals with thiols are similar; this suggests that most radicals derived from alkanes will have similar values of I_8 and the k_HI_8 values in Table I can be used as relative values of k_H. The isotope effects for the radicals derived from toluene, diphenylmethane, and triphenylmethane suggest that in a series of similar compounds some variation in I_8 will occur. Thus, for example, the k_HI_8 values for the series toluene, ethylbenzene, cumene or methanol, ethanol, isopropyl alcohol should be corrected for the variation in I_8 to obtain relative k_H data.

Table IV. Isotope Effects for the Reaction of $Q\cdot$ Radicals with Tritiated Thiols[a]

$Q\cdot$	k_H/k_T[b]
$C_6H_{11}\cdot$	3.2
$CH_3\cdot$	3.3
$C_6H_5CH_2\cdot$	10.7
$(C_6H_5)_2CH\cdot$	12.6
$(C_6H_5)_3C\cdot$	12.6

[a] Unpublished data of K. Kneipp. This is a partial list of the radicals studied, and we have also measured the temperature dependence of these isotope effects. All the data will be published later. [b] 60°.

Acknowledgments. W. A. Pryor wishes to thank Professors W. F. Libby and M. Calvin for hospitality during the tenure of a John Simon Guggenheim Fellowship, 1970–1971. We also wish to acknowledge helpful discussion with Professor Cheves Walling.

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(15) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York, N. Y., 1962, p 89.

(16) NOTE ADDED IN PROOF. In recent work we have found that the use of thiophenol does permit the study of a wide range of QH compounds. Using this thiol, the data for the hydrocarbons are largely unchanged but the three alcohols, methanol, ethanol, and isopropyl alcohol, give values which are in good agreement with data from our other methods: W. A. Pryor, T. Z. Lin, and J. P. Stanley, submitted for publication. Also see ref 2c and 2d.

(17) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959).