

Reactions of the Hydrogen Atom in Solution. IV. Photolysis of Deuterated Thiols^{1,2}

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Abstract: We here report a new method for studying the reactions of hydrogen atoms in solution which is simpler and more direct than previous methods. The hydrogen atoms are produced by the photolysis of thiols, and they react with organic hydrogen donors: $\text{QH} + \text{H}\cdot \rightarrow \text{Q}\cdot + \text{H}_2 (k_{\text{H}})$. For convenience in analysis, we actually used RSD and have studied the reactions of deuterium atoms. However, it is known that H and D atoms react with virtually the same rate constant, so that our data should be equivalent to data for the hydrogen atom. The technique used to obtain values of k_{H} involves measuring the HD to D₂ ratio produced as the QH to thiol solvent ratio is varied. The photolysis of thiols produces the thiyl radical as well as the hydrogen atom, but a series of control experiments has shown that the thiyl radical does not interfere with the analysis. Perhaps the most significant of these controls is that *tert*-butyl mercaptan and thiophenol, which have S-H bond dissociation energies differing by 13 kcal/mol, give results in excellent agreement. A comparison of our data with results obtained from the radiolysis of aqueous solutions shows excellent agreement for all compounds studied except ethanol and isopropyl alcohol. We also have obtained good agreement with our earlier data^{1,2} for saturated hydrocarbons obtained using tritiated thiols.

The hydrogen atom is a fascinating species. Its reactions have been used as a test of the predictive and calculational prowess of absolute rate theory for over 40 years,³ and this work continues today.⁴ From the viewpoint of a physical-organic chemist, it is the simplest homolog of the series of alkyl radicals which includes the much-studied methyl radical.^{1b,5} In addition, the hydrogen atom is a key species in radiation biology.⁶ Damage to cells by radiation is classed as either direct, in which the energy is transferred to an important biopolymer molecule directly, or indirect, in which the radiation produces reactive species in the aqueous region of the cell and these species diffuse to a biopolymer and react.⁷ The hydrogen atom is produced during the irradiation of either aqueous solutions or organic media; consequently, it could be important in causing damage by both mechanisms, and an intensive study has been made of model systems in which damage caused by the hydrogen atom can be identified.⁸

(1) (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. Rep.*, **4**, 98 (1970); (c) III: W. A. Pryor and M. G. Griffith, *J. Amer. Chem. Soc.*, **93**, 1408 (1971); (d) V: W. A. Pryor and R. W. Henderson, *ibid.*, **92**, 7234 (1970).

(2) (a) M. G. Griffith, Ph.D. Thesis, Louisiana State University, Jan 1968; (b) W. A. Pryor and M. G. Griffith, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper 15, section S; see also ref 1c.

(3) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941.

(4) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **40**, 2033 (1964); **43**, 3259 (1965); A. A. Westenberg and N. de Hass, *ibid.*, **47**, 1393 (1967); L. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *ibid.*, **48**, 2700 (1968); H. Conroy and B.L. Brumer, *ibid.*, **47**, 921 (1967). Also see references cited on p 151 of ref 5.

(5) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(6) (a) M. S. Blois, Jr., H. W. Brown, R. M. Lemmon, R. O. Lindblom, and M. Weissbluth, Ed., "Free Radicals in Biological Systems," Academic Press, New York, N. Y., 1961; (b) W. Snipes, Ed., "Electron Spin Resonance and the Effects of Radiation on Biological Systems," National Academy of Sciences, Washington, D. C., 1966.

(7) (a) A. P. Casarett, "Radiation Biology," Prentice-Hall, Englewood Cliffs, N. J., 1968; (b) Z. M. Bacq and P. Alexander, "Fundamentals of Radiobiology," 2nd ed, Pergamon Press, New York, N. Y., 1966.

(8) See, for example: (a) T. Henriksen, *Radiat. Res.*, **40**, 11 (1969); (b) B. H. Holmes, G. Navon, and G. Stein, *Nature (London)*, **213**, 1087

(1967); (c) G. Stein in "Energetics and Mechanisms in Radiation Biology," G. O. Phillips, Ed., Academic Press, New York, N. Y., 1968, p 467; (d) L. K. Mee, G. Navon, and G. Stein, *Biochim. Biophys. Acta*, **104**, 151 (1965); (e) H. Jung and K. Kurzinger, *Radiat. Res.*, **36**, 369 (1968); (f) A. A. Thannon, R. M. Peterson, and C. N. Trumbore, *J. Phys. Chem.*, **72**, 2395 (1968); (g) M. G. Ormerod and P. Riesz, *Biochim. Biophys. Acta*, **120**, 451 (1966).

Radiolysis of either aqueous solutions or organic media produces a number of reactive species including the electron, ions, and ion radicals, the hydrogen atom, molecular hydrogen, and, in aqueous solution, the hydroxyl radical and hydrogen peroxide.¹¹ Prior to 1960-1962, it was not recognized that both the electron and the hydrogen atom are produced in aqueous radiolysis, and consequently the kinetic data which were collected and ascribed to the action of the hydrogen atom alone may be in error.^{12,13} We will discuss some of these older data below. With the discovery of the solvated electron and the identification of its reactions by pulse radiolysis,¹⁴ some of the ambiguities were removed, and, presumably, data collected by the newer methods are reliable. In the gas phase and in pure water the hydrogen atom itself can be studied by pulse

(9) For a review of rate constants, see: M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(10) (a) J. K. Thomas in "Radiation Research 1966," North Holland Publishing Co., Amsterdam, 1967, pp 179-194; (b) C. L. Greenstock, J. W. Hunt, and M. Ng, *Trans. Faraday Soc.*, **65**, 3279 (1969).

(11) P. Ausloos, Ed., "Fundamental Processes in Radiation Chemistry," Interscience, New York, N. Y., 1968.

(12) (a) J. Rabani in "Solvated Electron," American Chemical Society Monograph No. 50, Washington, D. C., 1965, p 242; (b) R. A. Holroyd, *J. Phys. Chem.*, **70**, 1341 (1966); (c) C. E. Klotz, Y. Raef, and R. H. Johnsen, *ibid.*, **68**, 2040 (1964); (d) for a review, see P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).

(13) W. H. Hamill, *J. Phys. Chem.*, **73**, 1341 (1969).

(14) For a review see: (a) ref 10b; (b) G. Stein, "Radiation Chemistry of Aqueous Systems," Weizmann Science Press of Israel, Jerusalem, and Interscience, New York, N. Y., 1968.

radiolysis;¹⁵ however, in solution indirect methods have been used to follow the kinetics of H-atom reactions.⁹⁻¹⁴

In 1960-1962, Hardwick¹⁶ reported data for hydrogen atom reactions obtained by radiolysis of organic liquids. In one series of experiments^{16c} hexane was used as a standard hydrogen donor and the decrease in the yield of H₂ upon introduction of various solutes was measured. However, the electron is a precursor of hydrogen atoms in these systems so that any solute which scavenges electrons will diminish the yield of hydrogen gas. In recent years a number of workers have pointed out this limitation of Hardwick's technique.^{12b-d} Examination of Hardwick's relative rate constants themselves should have indicated that the data are not what would have been expected for a radical such as the hydrogen atom. For example, ethylbenzene was found to be more reactive than cumene, and *tert*-butyl mercaptan is relatively inert. The low reactivity of mercaptans is in conflict with a radiolysis study of ethyl mercaptan,¹⁷ and with all known data on free-radical reactions. This spurious result arises in Hardwick's system because of the great affinity mercaptans display for electrons.¹⁸

Clearly, it is highly desirable to study each of the reactive species produced by radiolysis independently, in the absence of the others, and to confirm the findings of the radiation studies. In particular, a number of methods not involving ionizing radiation have been discovered which produce hydrogen atoms. For example, in the gas phase the photolysis of hydrogen sulfide and thiols has been used,¹⁹ and the photolysis of HI in hexane also has been briefly described.^{19g} The most frequently used method at present involves passing a stream of hydrogen gas past a discharge and then allowing this H-atom enriched gas to bubble through the solution to be studied.²⁰ This method has

(15) (a) P. Pagsberg, H. Christensen, J. Rabani, G. Nilson, J. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, **73**, 1029 (1969); (b) J. W. Boyle, J. A. Ghormley, C. J. Hochanadel, and J. F. Riley, *ibid.*, **73**, 2886 (1969).

(16) T. J. Hardwick, *ibid.*, (a) **64**, 1623 (1960); (b) **65**, 101 (1961); (c) **66**, 117, 291 (1962).

(17) J. J. Myron and R. H. Johnsen, *ibid.*, **70**, 2951 (1966).

(18) A. El Samahy, H. L. White, and C. N. Trumbore, *J. Amer. Chem. Soc.*, **86**, 3177 (1964); D. A. Armstrong and V. G. Wilkening, *Can. J. Chem.*, **42**, 2631 (1964).

(19) In much of this gas-phase work, the hydrogen atom is "hot" (i.e., excited by more than RT translational energy) and, consequently, reacts indiscriminately. These studies, therefore, have a very different viewpoint than do ours in solution where the hydrogen atom has thermal energy. See: (a) L. E. Compton, J. L. Gole, and R. M. Martin, *J. Phys. Chem.*, **73**, 1158 (1969); (b) G. P. Sturm and J. M. White, *ibid.*, **72**, 3679 (1968); (c) G. R. Woolley and R. J. Cvetanovic, *J. Chem. Phys.*, **50**, 4697 (1969); (d) R. J. Cvetanovic and L. C. Doyle, *ibid.*, **50**, 4705 (1969); (e) G. P. Sturm, Jr., and J. M. White, *J. Phys. Chem.*, **72**, 3679 (1968); *J. Chem. Phys.*, **50**, 5035 (1969); J. M. White and G. P. Sturm, Jr., *Can. J. Chem.*, **47**, 357 (1969); (f) D. M. Graham, R. L. Mielville, and C. Sivertz, *ibid.*, **42**, 2239 (1964); D. M. Graham and J. F. Soltys, *ibid.*, **47**, 2529 (1969); D. M. Graham and J. F. Soltys, *ibid.*, **47**, 2719 (1969); (g) D. Perner and R. H. Schuler, *J. Phys. Chem.*, **70**, 317 (1966); (h) also see these papers on cysteine: H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, **45**, 809 (1966); D. B. Peterson, H. Holian, and W. M. Garrison, *J. Phys. Chem.*, **73**, 1568 (1969); W. F. Forbes and J. V. Ramsbottom, *Nature (London)*, **216**, 913 (1967); W. Wolf, J. C. Kertesz, and W. C. Landgraf, *Spectrosc. Lett.*, **1**, 27 (1968); V. G. Wilkening, M. Lal, M. Arends, and D. A. Armstrong, *Can. J. Chem.*, **45**, 1209 (1967); D. H. Volman, J. Wolstenholme, and S. G. Hadley, *J. Phys. Chem.*, **71**, 1798 (1967); D. H. Volman, *J. Chem. Phys.*, **46**, 1541 (1967).

(20) (a) The early references are summarized by H. Jensen and T. Henriksen, *Acta Chem. Scand.*, **22**, 2263 (1968); (b) G. Navon and G. Stein, *Israel J. Chem.*, **2**, 151 (1964); (c) F. G. Liming, Jr., *Radiat. Res.*, **39**, 252 (1969).

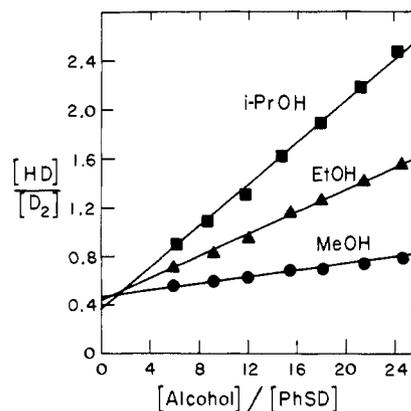
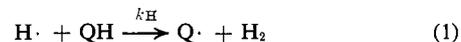


Figure 1. Plot of eq I. Data obtained for alcohols and thiophenol; the alcohols were deuterated to prevent exchange with the thiols.

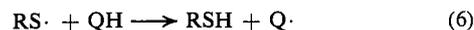
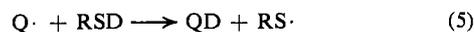
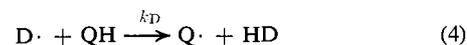
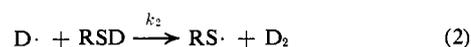
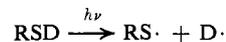
produced valuable data, but is kinetically quite complex.²¹

Some years ago² we initiated a program to produce the hydrogen atom by techniques not involving ionizing radiation and to study its reactions in solution. We here wish to report the photolysis of thiols in solution to yield hydrogen atoms and the determination of the relative rate constants for reaction of this species with a number of organic compounds. It is well known that thiols can be photolyzed to produce hydrogen atoms,¹⁹ and in our system these react with QH to produce H₂.



Results

When mixtures of deuterated thiols, RSD, and hydrogen donors, QH, are photolyzed, the following reactions can occur



where $\cdot\text{RSD}$ is a thiol which has lost a hydrogen atom from its alkyl group. By limiting the reaction to low conversions, reactions 5, 6, and 7 can be neglected. (Reaction 6 is endothermic and therefore slow for most QH compounds we have studied.) A steady-state kinetic analysis of this scheme shows that

$$\frac{[\text{HD}]}{[\text{D}_2]} = \frac{k_3}{k_2} + \frac{k_{\text{H}}I}{k_2} \frac{[\text{QH}]}{[\text{RSD}]} \quad (I)$$

where $I = k_{\text{D}}/k_{\text{H}}$ and is the isotope effect on reactions 1 and 4. It can be seen that a plot of $[\text{HD}]/[\text{D}_2]$ vs. $[\text{QH}]/[\text{RSD}]$ should yield a straight line of slope $k_{\text{H}}I/k_2$ and intercept k_3/k_2 . Typical plots of eq I are shown in Figure 1 for methanol, ethanol, and 2-propanol with thiophenol.²²

(21) G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1384 (1965).

(22) The alcohols were deuterated in the O-H position so that ex-

Our initial experiments with this system indicated the existence of some complicating reactions which could conceivably invalidate the above kinetic analysis. However, subsequent investigations proved these potential problems to have a negligible effect on the measured relative rates (see Experimental Section).

One feature of our system is worthy of special consideration. Photolysis of thiols generates both hydrogen atoms and thiyl radicals, and it is possible that the presence of these latter species might invalidate the kinetic analysis leading to eq 1. If the thiyl radical affected our values of k_{HI} , then the use of thiols of very different S-H bond strengths should produce very different results, since the reactivity and selectivity of the thiyl radical depends on the strength of the S-H bond. In fact, all of the reactions in the above scheme except reactions 3 and 4 depend on the S-H or S-S bond strength of the thiol or its disulfide. We therefore performed a parallel series of experiments in which either thiophenol or *tert*-butyl mercaptan (which have a 13-kcal/mol difference in S-H dissociation energies)²³ was photolyzed with some 15 organic hydrogen donors. These data are listed as relative rate constants (hexane = 1.0) in Table I. Comparison of the values in columns

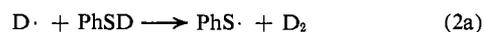
Table I. Relative Rate Constants for Hydrogen Abstraction by Deuterium Atoms

QH	(CH ₃) ₂ CSD k_{HI} , rel ^a	PhSD k_{HI} , rel ^b	Ave ^c k_{HI} , rel
Hexane	(1)	(1)	(1)
Nonane	2.37	1.98	2.18 ± 0.20
Dodecane	2.10	2.54	2.32 ± 0.22
2,3-Dimethylbutane	2.17	2.24	2.21 ± 0.04
2,4-Dimethylpentane	1.54	1.35	1.45 ± 0.10
2,5-Dimethylhexane	2.22	2.60	2.41 ± 0.19
Cyclohexane	1.25	1.10	1.18 ± 0.08
Cyclopentane	1.28	1.09	1.18 ± 0.09
Methanol	0.50	0.33	0.42 ± 0.09
Ethanol	1.04	1.27	1.16 ± 0.11
2-Propanol	1.82	2.00	1.91 ± 0.09
2-Methyl-2-propanol	0.03	0.02	0.03 ± 0.01
Dioxane	2.74	3.18	2.96 ± 0.22
Tetrahydrofuran		9.05	9.05
Diethyl ether	4.72	5.15	4.94 ± 0.22
Diisopropyl ether	5.26	4.26	4.76 ± 0.50

^a For hexane $k_{HI}/k_2 = 0.062$. ^b For hexane $k_{HI}/k_2 = 0.056$. ^c Average of columns two and three; difference between average value and measured values shown as ± numbers.

two (*tert*-butyl mercaptan) and three (thiophenol) shows that the data from the two thiols agree extremely well over a range of reactivities of over 100. (The average agreement is ±10%.) It seems quite unlikely that this agreement would be observed if eq 1 were not an accurate representation of our system. This finding, together with the other control experiments reported in the Experimental Section, indicates

change with the thiol would not produce RSH. For thiophenol, reactions 2 and 3 should be replaced by



where the radicals in parentheses are cyclohexadienyl radicals.

(23) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

that our system is capable of yielding reliable relative rate constants for hydrogen atom abstraction reactions from various hydrogen donors.

Discussion

Isotope Effects. Before proceeding to a comparison of our results with previous data, it will be useful to discuss the isotope effects in our system. Our work measures abstraction reactions of the deuterium atom while previous workers have studied the reactions of the hydrogen atom. Anbar and Meyerstein²⁴ have stated: "It is generally accepted that the rates of reaction of H and D atoms with different substrates are equal." This is expected because zero-point energy differences in the transition state will be small and the H· and D· reactants have no zero-point energy. The isotope effect in these reactions will largely arise from MMI and EXC terms in the Bigeleisen equation²⁵ and should be fairly independent of the strength of the QH bond. At 1000°K and in the gas phase, conditions admittedly quite different from our own work, rates have been measured²⁶ for hydrogen and deuterium atom reactions with H₂ (1.1 and 0.98 × 10⁹ M⁻¹ sec⁻¹) and D₂ (0.57 and 0.61 × 10⁹ M⁻¹ sec⁻¹) and no significant isotope effect is observed. Also, examination of measured or calculated values for the above reactions at 300°K reveals a multitude of rate constants,²⁷ but the values obtained by any single group of workers indicates that in no case is an isotope effect greater than about two for hydrogen or deuterium atom reactions with H₂ observed. It seems certain that any isotope effect in our system is small and the variation of the isotope effect with QH will be even smaller. Therefore, we feel that our relative values of k_{HI} can be compared directly with literature data on the hydrogen atom.

Previous Data. Data for hydrogen abstraction reactions by hydrogen atoms are available from several sources. We will review these systems briefly, and in the following sections we will compare these literature data to our own. The greatest amount of work has been reported for the radiolysis of aqueous solutions.^{9,10a,13,28} The relative rate constants for hydrogen abstraction by hydrogen atoms obtained in these systems are found to be in excellent agreement among the various laboratories. Hydrocarbon radiolysis data, both gas and liquid phase,^{12b,16,21,29-32} appear to be less precise and extensive. The most complete, self-consistent set of data from a single laboratory for the attack of the hydrogen atom on hydrocarbons in the gas phase is the data of Holroyd, *et al.*³³ These workers

(24) M. Anbar and D. Meyerstein in "Radiation Chemistry of Aqueous Systems," G. Stein, Ed., Interscience, New York, N. Y., 1968, p 116.

(25) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958); M. Wolfsberg and M. J. Stern, *J. Pure Appl. Chem.*, **8**, 225, 325 (1964).

(26) G. Boato, G. Careri, A. Cimino, E. Molinari, and G. C. Volpi, *J. Chem. Phys.*, **24**, 783 (1956).

(27) (a) J. Hirschfelder, H. Eyring, and B. Topley, *ibid.*, **4**, 170 (1936);

(b) W. R. Schulz and D. J. LeRoy, *Can. J. Chem.*, **42**, 2480 (1964);

J. Chem. Phys., **42**, 3869 (1965); (c) I. Shavitt, *ibid.*, **31**, 1359 (1959);

(d) A. A. Westenberg and N. de Hass, *ibid.*, **47**, 1393 (1967).

(28) R. R. Hentz, Farhatziz, and D. J. Milner, *ibid.*, **49**, 2153 (1968).

(29) G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968).

(30) (a) R. H. Holroyd in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968,

Chapter 7; (b) B. A. Thrush, *Progr. React. Kinet.*, **3**, 64 (1965).

(31) F. G. Liming, Jr., *Radiat. Res.*, **39**, 252 (1969).

(32) K. Yang, *J. Phys. Chem.*, **67**, 562 (1963).

(33) (a) R. A. Holroyd and G. W. Klein, *ibid.*, **67**, 2273 (1963);

Table II. Comparison of Relative Rate Data for Alcohols and Ethers

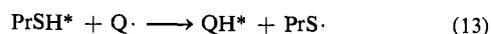
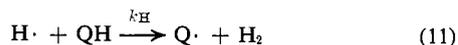
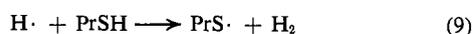
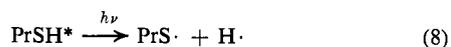
No.	QH	N ^a	Present ^b		P & G ^c		Aq radiolysis ^d	
			Per mole	Per H ^e	Per mole	Per H ^e	Per mole	Per H ^e
1	CH ₃ OH	3	(1)	(1)	(1)	(1)	(1)	(1)
2	CH ₃ CH ₂ OH	2	2.8	4.2	12.2	18.4	9.4	14.3
3	<u>OCH₂CH₂OCH₂CH₂</u>	8	7.2	2.7	3.4	1.3	3.1	1.2
4	<u>OCH₂CH₂CH₂CH₂</u>	4	22.5	16.5			18	14
5	(CH ₃ CH ₂) ₂ O	4	12	9.0				
6	HOCH ₂ CH ₂ OH	4					5	3.8
7	HOCH ₂ CH ₂ CH ₂ OH	4					10	7.6
8	(CH ₃) ₂ CHOH	1	4.7	14.1	39.8	120.0	30.2	92
9	([CH ₃] ₂ CH) ₂ O	2	11.6	17.4				
10	(HOCH ₂) ₂ CHOH	1					10.6	17 ^f
11	HOCH ₂ (CHOH) ₂ CHO	5					21	11 ^{f,g}
12	(CH ₃) ₃ COH	9	0.073	0.024			0.062	0.021

^a Number of reactive hydrogens. ^b $k_{\text{H}}I$, relative. Present work. ^c $k_{\text{H}}I'$, relative. Work of Pryor and Griffith, see text. ^d Average values of data reviewed in M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967), and of R. R. Hentz, Farhataziz, and D. J. Milner, *J. Chem. Phys.*, **49**, 2153 (1968). ^e Calculated assuming only the italicized hydrogens are reactive. ^f Calculated assuming the secondary hydrogens to be the same reactivity as those in glycol. ^g Calculated assuming aldehyde proton to be the same reactivity as other italicized hydrogens.

obtained rates of abstraction by hydrogen atoms relative to the addition of the hydrogen atom to ethylene. The discharge method²⁰ has not as yet been applied to a series of simple organic compounds; instead work of this type has concentrated on biopolymer molecules.

Some of the radiolysis-derived data of Hardwick¹⁶ were discussed in the introductory section, and it was pointed out that systematic errors occur due to reaction of the solvated electron. However, one of the systems which Hardwick examined^{16b} involved the use of methyl methacrylate as a standard hydrogen atom scavenger and a range of alkanes as hydrogen donors. The alkanes all have similar, low-electron affinities, and this system may yield true values of k_{H} for alkanes. Dilute solutions of methyl methacrylate in alkanes were irradiated, and the variation in the yield of H₂ was studied as a function of the scavenger concentration. The data from this system are self-consistent and yield reasonable values for the reactivity of different types of hydrogen atoms.

Pryor and Griffith² have reported a system for measuring the relative rate constants of hydrogen atom reactions in solution by a technique not involving ionizing radiation. Their method involved the photolysis of tritiated thiols; a simplified reaction scheme is shown below for the thiol they used, propyl mercaptan,



where EtCH₂*SH is alkyl-labeled thiol and QH* is recovered, tritiated substrate. Kinetic analysis² yields an equation which indicates that values of $k_{\text{H}}I'$ can be obtained by measuring the rate of incorporation of tritium into QH as a function of the [QH]/[PrSH] ratio, where I' is the isotope effect $k_{\text{T}}/k_{\text{H}}$ for reaction 13.

(b) R. A. Holroyd and T. E. Pierce, *J. Phys. Chem.*, **68**, 1392 (1964);
(c) R. A. Holroyd, *ibid.*, **70**, 1341 (1966).

Values of I' for several Q· radicals have been measured,³⁴ and, as might be expected,³⁵ I' does depend on the structure and reactivity of the organic radical. However, the I' values within a series of similar QH compounds (*e.g.*, the alkanes) should be fairly constant.

Alcohols and Ethers. It will be most instructive to consider the data for alcohols and ethers apart from the hydrocarbon data. Our present results, obtained from column 4 of Table I, are compared with the previous data of Pryor and Griffith² and aqueous radiolysis data^{9,28} in Table II. The data are given as rate constants relative to the rate of abstraction from methanol, both per mole, as measured, and per reactive hydrogen.

The data in Table II show that our values agree well with the values of the previous two methods for all compounds except ethanol and 2-propanol. It should be noted that both of the thiol-photolysis methods give the same rate for methanol, relative to hexane (0.42 for the present work and 0.42 for Pryor and Griffith). The most revealing way to view relative rate constants is on a per-hydrogen basis, because only in this way can the rate constants be compared for similar reactive centers. Examination of entries 2–7 in Table II (compounds containing the RCH₂OR' group) reveals a range of reactivities much greater than would have been expected in view of the minor differences in the electronic and structural variations within these compounds. The reactivities of ethanol (as measured by Pryor and Griffith and radiolysis) and THF (as measured in the present work and radiolysis) appear much higher than the other similar compounds. A relative reactivity of about 5 seems most reasonable for compounds 2–7. Turning now to compounds containing the R₂CHOR' group (entries 8–11 in Table II), a wide range of reactivities is again observed. The reactivity of 2-propanol as obtained by both radiolysis and by Pryor and Griffith appears to be surprisingly large compared to the values obtained in the present work and other compounds containing the same reactive center. The best value for such tertiary hydrogens appears to be 14 ± 3 .^{35a}

(34) Unpublished data of K. Kneipp cited in (a) W. A. Pryor and T. F. Fiske, *Intrasci. Chem. Rept.*, **3**, 249 (1969); and (b) W. A. Pryor and U. Tonellato, *J. Phys. Chem.*, **73**, 850 (1969).

(35) See ref 5, p 162 ff.

In summary, there are several discrepancies in the data for alcohols and ethers, both among the various methods and for different compounds measured by the same method. The previous methods indicate that ethanol and 2-propanol have an unusually high reactivity compared with analogous compounds. It is certainly quite surprising that the hydrogen atom shows the same reactivity pattern in aqueous solution as in organic media toward most compounds, but quite a different reactivity toward ethanol and 2-propanol in the two media. This does not appear to be a solvent effect since in the system used here the addition of up to 50 mol % water (as D₂O), the limit of miscibility, to mixtures of thiophenol and 2-propanol does not change the relative rate measured.

The system of Pryor and Griffith² has the disadvantage of measuring secondary products of the abstraction reaction instead of the primary products as is done in the present work. Their method will give erroneous results if any species other than the hydrogen atom abstracts from QH to produce Q· radicals. Calculations using known rate constants for models of the steps involved suggest that the thiyl radical could attack QH in cases where the Q-H bond strength is equal to or lower than the RS-H bond strength.³⁶ This could occur for 2-propanol and possibly for ethanol as well.³⁶ Because of this we will omit from our subsequent discussion the data on oxygen compounds determined by the method of Pryor and Griffith.^{35a}

Hydrocarbons. The relative rate constants for hydrogen abstraction from several hydrocarbons, as obtained by various workers, are listed in Table III. An explanatory note is necessary about this table. Both because the experimental uncertainties in the values for any particular compound confuse the comparisons, and because all workers did not study the identical series of compounds, calculated values are tabulated rather than the raw data themselves. The calculated values were obtained by using the relative reactivities of primary, secondary, and tertiary hydrogens shown at the bottom of the table; these latter values were obtained as average values from selected compounds studied by each method.³⁷ The values listed for primary, secondary, and tertiary hydrogens from Hardwick's^{16b} work are those reported by the author. The values listed for Holroyd's³³ work were calculated by us using propane, pentane, hexane, and

(35a) NOTE ADDED IN PROOF. In recent work we have found that the use of thiophenol instead of propanethiol in the method of Pryor and Griffith leads to values for methanol, ethanol, and isopropyl alcohol which agree very well with the data obtained by the RSD method reported here: W. A. Pryor, T. Z. Lin, and J. P. Stanley, submitted for publication.

(36) The bond strength of the α -CH bond in 2-propanol can be estimated to be 85 kcal/mol (S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968). The S-H bond strength for propyl mercaptan is 88 kcal/mol²³ and therefore the reaction $RS\cdot + (CH_3)_2CHOH \rightarrow RSH + (CH_3)_2\dot{C}OH$ is nearly thermoneutral. Similar reactions have been studied in some detail (R. M. Kellogg in "Methods in Free Radical Chemistry," E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, pp 108-110; C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959)).

(37) The necessity of using as many experimental values as possible can be seen from the following example using our own data. If only hexane and dodecane are used to calculate the ratio of reactivities of primary to secondary hydrogens, a value of 1:5.5 is obtained. If the relative reactivity of dodecane is increased by 5% (within experimental error) this ratio changes to 1:18. Clearly, precise data for a wide range of carefully selected compounds are necessary in order to derive meaningful primary to secondary to tertiary reactivities. Even in these cases these data may be accurate to no more than 10%.

Table III. Comparison of Relative Rate Constants for the Reaction of Hydrocarbons with the Hydrogen Atom in the Gas and Liquid Phase^a

QH	Radiolysis ^b liq	Radiolysis- ^c photolysis gas	Photolysis	
			RSD ^d liq	RSH(T) ^e liq
Pentane	0.78	0.79	(0.87)	
Hexane	[1]	[1]	[1]	[1]
Heptane	1.23	(1.24)	(1.30)	
Octane	1.45	(1.47)	(1.50)	
Nonane	1.67	(1.70)	1.66	
Dodecane	(2.34)	(2.37)	2.32	2.28
Cyclopentane	1.12	1.13 ^f	1.09	
Cyclohexane	(1.35)	1.37 ^f	1.31	1.28
2,2-Dimethylbutane	0.43	0.45	(0.48)	
2-Methylpentane	2.10	2.58	(1.56)	
2,3-Dimethylbutane	3.21	4.17	2.09	1.96
2,4-Dimethylpentane	3.43	4.40 ^f	2.31	
2,5-Dimethylhexane	(3.65)	(4.63)	2.53	
Primary ^g	0.017	0.019	0.022	0.023
Secondary ^g	0.112	0.113	0.109	0.107
Tertiary ^g	1.50	1.97	0.915	0.84

^a All data relative to hexane; values in parentheses represent compounds not investigated by that method. All relative reactivities are calculated values obtained using data at bottom of table so experimental inconsistencies do not confuse the comparisons. ^b T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961). Liquid phase radiolysis, 25°. See text. ^c R. A. Holroyd, *et al.*, *J. Phys. Chem.*, **67**, 2273 (1963); **68**, 1392 (1964); **70**, 1341 (1966). Gas-phase radiolysis and mercury-photosensitized decomposition of alkanes, 25°. See text. ^d Present work. ^e Values listed are the average of the values obtained using propanethiol² and the values obtained with thiophenol (unpublished data of W. A. Pryor, J. P. Stanley, and T. H. Lin). ^f Data obtained in the liquid phase. ^g Relative reactivities, per hydrogen, of primary, secondary, and tertiary hydrogens are reported on a scale of hexane = 1.00, so the reactivities in the upper part of the table can be calculated directly from these data.

2,2-dimethylbutane for primary and secondary hydrogen reactivities and isobutane, 2-methylbutane, 2-methylpentane, and 2,3-dimethylbutane for tertiary hydrogens. The values for our own work were calculated using hexane, dodecane, cyclopentane, and cyclohexane for primary and secondary hydrogens and 2,3-dimethylbutane and 2,5-dimethylhexane for tertiary hydrogens.

Examination of the data in Table III will indicate the rather good agreement among the various methods for all compounds containing only primary and secondary hydrogens. For compounds containing tertiary hydrogens, the values obtained in the present work are seen to be about 30% lower than the values obtained by Hardwick.^{16b} Hardwick's data have been criticized by Holroyd^{33c} who has pointed out that if the electron is scavenged by low methyl methacrylate concentrations, Hardwick's data will be in error in the sense that compounds containing only primary and secondary hydrogens will have a reactivity too low compared with compounds containing tertiary hydrogens. Table III also compares data on alkanes from this laboratory determined by the method of Pryor and Griffith² using tritiated thiol. The data for this method appearing in Table III are the average of the values using propanethiol² and more recent values obtained using thiophenol.³⁸

Selectivities. It is instructive to compare the selectivities of hydrogen atoms, obtained by the various methods, with other free radicals toward various types

(38) The results using propanethiol and thiophenol are in good agreement for the alkanes which have been tested.

Table IV. Relative Rate Constants for the Reaction of Various Radicals with Hydrogens of Different Types^a

	—H—		—CH ₃ —		RCH ₂ · Org phase, 130° ^f	C ₆ H ₅ · Org phase, 60° ^g
	Thiol, ^b 35°	Radiolysis, ^c 25°	Gas phase, 182° ^d	Aq solu- tion, 25° ^e		
Alcohols						
CH ₃ OH	(1) ^h	(1) ⁱ	(1) ^j	(1)	(1)	(1) ^k
CH ₃ CH ₂ OH	4.2 ^h	15 ⁱ	5 ^j	5	5	3 ^k
(CH ₃) ₂ CHOH	14 ^h	92 ⁱ	25 ^j	46	20	9 ^k
Alkanes						
Primary H	(1) ^l	(1) ^m	(1) ⁿ		(1) ^o	(1)
Secondary H	5 ^l	6 ^m	5 ⁿ		3 ^o	9
Tertiary H	40 ^l	96 ^m	33 ⁿ			44

^a On a per hydrogen basis. ^b Photolysis of mixtures of thiol and hydrogen donor. ^c Radiolysis methods; aqueous solution for alcohols and gas or organic phase for alkanes. ^d We feel that extrapolation of these data to room temperature is unreliable. ^e J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967). ^f G. A. Mortimer, *J. Polymer Sci., Part A-1*, **4**, 88 (1966). ^g R. R. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963). ^h Data obtained using the RSD method only. ⁱ M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967). See Table II. ^j A. A. Herrod, *Chem. Commun.*, 891 (1968); CD₃· radical. ^k G. A. Russell, unpublished data presented in the Free Radical Symposium at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. The values are for phenyl ethers instead of alcohols. ^l Average values taken from columns 4 and 5 in Table III. ^m Average values taken from columns 2 and 3 in Table III (data of Hardwick and of Holroyd). ⁿ W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962); data obtained using empirical relationship developed by the authors. ^o Values calculated using butane, pentane, hexane, decane, and tridecane data. Too few compounds containing tertiary hydrogens were studied to yield reliable value.

of hydrogen donors. These data are collected in Table IV. The data for alcohols show that the radiolysis data make the hydrogen atom appear to be more selective than either the methyl, polymethylene, or phenyl radical. By contrast, our present data show the selectivity of the hydrogen atom to be midway between the methyl and polymethylene radicals and the phenyl radical. The hydrogen atom is found to be somewhat more selective toward the hydrocarbons than toward the alcohols in the present work. This is as would be expected, since the alcohols are more reactive;³⁹ the other radicals exhibit this same selectivity pattern. The hydrocarbon radiolysis data also indicate a higher selectivity for the hydrogen atom than the methyl radical, whereas our data and that of Pryor and Griffith² agree well with the data for methyl and phenyl radicals.

Structural Features and Reactivity. The relative reactivity obtained in this work for the dimethyl-substituted alkanes shows an unexpected low reactivity for 2,4-dimethylpentane. This also was observed for hydrogen abstraction by phenyl radicals by Bridger and Russell⁴⁰ who suggested that the unreactivity of 2,4-dimethylpentane results from the preferred con-

(39) Each hydrogen on methanol is 4.5 times as reactive as a primary hydrogen on hexane. The correlation of reactivity and selectivity should be made with caution, however. The rate of hydrogen abstraction by a radical may be governed by factors not greatly dependent upon bond strength, such as a different preexponential factor (S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968), solvent effects (W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 157), or polar factors. It is noteworthy that the methyl and phenyl radicals have been shown to have about the same ρ value (W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969); ref 40).

(40) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

formation of this compound which places both tertiary hydrogens in close proximity. The ratios of the experimental to calculated reactivity for 2,3-dimethylbutane, 2,4-dimethylpentane, and 2,5-dimethylhexane were found by Bridger and Russell to be 1.21, 0.58, and 0.95, respectively.⁴⁰ Our data yield experimental to calculated reactivity ratios of 1.06, 0.63, and 0.95. (Holroyd's³³ data seem to show this effect, but Hardwick's^{16b} do not.) The agreement between our data for the H atom and the data for the phenyl radical is better than might be expected if steric hindrance to attack were important since the steric requirements of the phenyl radical and the hydrogen atom should be quite different. Thus, the reactivity order must be the result of the number of productive directions of attack on the alkane and of conformational factors.

Bridger and Russell⁴⁰ also found the relative reactivity (per hydrogen) of cyclopentane to be 1.15 times that of cyclohexane. Our work indicates the cyclopentane hydrogens to be 1.20 times as reactive as cyclohexane hydrogens.

Summary. Our system for studying hydrogen atom reactions is by far the simplest, both chemically and experimentally, of the methods previously reported. The data obtained in the present system agree very well with most of the previous data on hydrogen atom reactions. Indeed, we find a major discrepancy for only two of the compounds studied. Our data are self-consistent, both for the hydrocarbons and for the alcohols and ethers, and indicate a selectivity for the hydrogen atom in reasonable agreement with expectations based on the selectivities of other radicals. Work is continuing in this and similar systems in hopes of elucidating the chemistry of the hydrogen atom more thoroughly.

Experimental Section

All hydrocarbons were stirred with H₂SO₄, dried, and distilled. Deuterated thiols were prepared by stirring the thiol with portions of D₂O until greater than 98% deuteration was indicated by the nmr spectra. The thiols were subsequently dried and periodically distilled. All alcohols used were also deuterated at the O-H position in a similar manner.

Mixtures of thiols (RSD) and hydrogen donor (QH) were prepared, degassed, and photolyzed in quartz tubes for 1 hr at 35° in a Rayonet photochemical reactor equipped with a "merry-go-round" to ensure uniform light intensity (using the "3000 Å" lamps from Rayonet). The solutions were then degassed directly into a CEC Model 21-620 mass spectrometer and the ratios of mass 3-4 were analyzed. These ratios were then converted to [HD]/[D₂] ratios by a sensitivity factor ratio obtained from known mixtures of HD and D₂. The yields of disulfide, RSSR, assumed to be a measure of the extent of reaction, were obtained by gas chromatography.

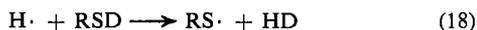
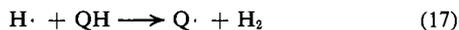
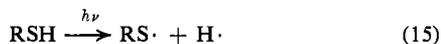
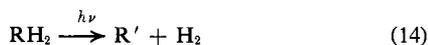
Our initial experiments with this system revealed three potential difficulties in obtaining reliable rates. Subsequent study of these problems has shown that in fact they have a negligible effect on the measured relative rates. Each of these problems will be discussed in turn.

Concentration Ranges. Our preliminary studies gave plots of [HD]/[D₂] vs. [QH]/[RSD] which displayed a slight but definite negative deviation at [QH]/[RSD] values below about 5, and a measured intercept at [QH] = 0 considerably below the value extrapolated from the straight-line portion of the curve. Plots similar to Figure 1 for all compounds studied gave good straight lines for [QH]/[RSD] between 6 and 24, but at [QH]/[RSD] between 0 and 5, a line of different slope and slight curvature was obtained. This curvature was such that a straight line could approximate the data rather well, so that two values of k_{H}/k_2 could be obtained—one at the low [QH]/[RSD] range and another, smaller value at the higher range.

Relative values of k_{HI} for cyclohexane and dodecane were obtained in both concentration ranges with propyl mercaptan, *tert*-butyl mercaptan, and thiophenol. In the high [QH]/[RSD] range, all thiols gave, within experimental error, the same k_{HI} for dodecane, relative to cyclohexane, but in the low range the values were widely scattered. From the same data, values of k_2 for thiophenol and propyl mercaptan could be obtained, relative to *tert*-butyl mercaptan, in both cyclohexane and dodecane. Again it was found that the precision and internal consistency of these values were much higher in the high [QH]/[RSD] range than in the low range.

The observation that all three thiols give the same relative k_{HI} values at the high QH to thiol concentration range is quite significant (see Results). Thus, the agreement of the relative rates with the different thiols, the greater precision, and the straight lines obtained with the high [QH]/[RSD], dilute thiol, runs indicate that eq I is valid under these conditions. The reason for the deviation in the low [QH]/[RSD] range is not clear although one can envision several kinetic complications being important in this range. A somewhat similar observation has been made in the gas-phase photolysis of D_2S and alkanes.⁴¹

H₂ Formation. The second potential difficulty is the observation that a larger amount of H₂ is formed than might have been expected from the approximately 2% RSH present in the RSD. The amount of H₂ formed was found to be about 8–20% of the total H₂ + HD + D₂. The amount of H₂ produced has been found to vary ($\pm 6\%$), although not in a simple way, with the nature of QH and the [QH]/[RSD] ratio. The possible modes of H₂ formation are shown in eq 14–18, where RH₂ is any compound containing two



hydrogens, and RSH is either an impurity in the RSD or is produced during the course of the photolysis by, for instance, reaction of RS· with a hydrogen donor.

If reaction 14 is the source of H₂, then our previous kinetic analysis would be unaffected. If, on the other hand, H₂ arises from reactions 15–17, then reaction 18 also would be expected to occur and our previous kinetic analysis will be in error. When reactions 16–18 are included in the mechanism, eq I must be replaced with eq II. Similarly, eq III also is obtained. Examination of eq II

$$\frac{[HD]}{[D_2]} = \frac{k_3}{k_2} + \frac{k_{HI}}{k_2} \frac{[QH]}{[RSD]} + \frac{k_{18}}{k_2} \frac{[H\cdot]}{[D\cdot]} \quad (II)$$

$$\frac{[H_2]}{[D_2]} = \frac{k_{16}}{k_2} \frac{[H\cdot]}{[D\cdot]} + \frac{k_{17}}{k_2} \frac{[H\cdot]}{[D\cdot]} \frac{[QH]}{[RSD]} \quad (III)$$

reveals the fact that if $[H\cdot]/[D\cdot]$ is constant for any given QH at all [QH]/[RSD] values, then a plot of $[HD]/[D_2]$ vs. $[QH]/[RSD]$ will still yield a straight line of slope k_{HI}/k_2 , but the intercept is now $k_3/k_2 + (k_{18}/k_2)([H\cdot]/[D\cdot])$. This condition appears reasonable if H· arises only from photolysis of RSH and if reaction 6 is slow; reaction 6 probably is slow for most QH compounds (see below).

The constancy of $[H\cdot]/[D\cdot]$ can be tested in the following way. Examination of eq III shows that a plot of $[H_2]/[D_2]$ vs. $[QH]/[RSD]$ will yield a straight line if $[H\cdot]/[D\cdot]$ is constant throughout the thiol concentration range. Experimentally it is found that straight lines are indeed found for every QH compound studied. (The points are somewhat more scattered than the $[HD]/[D_2]$ plots, probably due to the smaller amount of H₂ being measured.) Thus, even if eq II is more correct than eq I, plots such as in Figure 1 should still yield reliable k_{HI} values.

(41) B. de B. Darwent and R. Roberts, *Discuss. Faraday Soc.*, **14**, 55 (1953).

In another test of the importance, of RSH impurity in the RSD, 10% PhSH was added to PhSD, this mixture was photolyzed with cyclohexane and with dodecane, and k_{HI}/k_2 values were obtained. Although these runs lead to the formation of twice as much H₂, the k_{HI}/k_2 values were the same as obtained in the absence of added PhSH, within experimental error. Similarly, it was found that addition of as much as 50 mol % D₂O to a mixture of 2-propanol-*d*₁ and thiophenol-*d*₁ reduced the per cent of H₂ by half but the apparent k_{HI}/k_2 was unaffected. Therefore, although we are uncertain as to the origin of the H₂, it is clear that our measurement of relative k_{HI} values is unaffected by its formation.

Disulfide Formation. The third potential difficulty with this system is the formation of disulfide *via* reaction 7. It was hoped that the experiments could be limited to low conversions where the yields of disulfide would be negligible. However, to achieve sufficient gas pressures at the concentrations and scale used in the experiments, conversions of 5–15% had to be studied. The disulfide can enter our kinetic scheme in the following ways (eq 19 and 20). If reaction 20 is incorporated into the kinetic scheme of



reactions 2–7, we obtain

$$\frac{[HD]}{[D_2]} = \frac{k_3}{k_2} + \frac{k_{20}}{k_2} \frac{[RSSR]}{[RSD]} + \frac{k_{HI}}{k_2} \frac{[QH]}{[RSD]} \quad (IV)$$

This equation shows that if $[RSSR]/[RSD]$ is not constant at the various [QH]/[RSD] ratios used, then our values of the slope of plots of eq I will not be equal to k_{HI}/k_2 . Analysis of reaction mixtures showed that $[RSSR]/[RSD]$ was not constant at the various thiol concentrations used; the yield of RSSR was found to vary from about 5 to 15% in the most extreme cases. Generally, more RSSR was found at the lower thiol concentrations.⁴² The most likely explanation for the varying relative yields of disulfide can be seen from reaction 19. It is known that $k_{19} > k_{HI}$.⁴³ For runs with low thiol and high QH concentrations, QH competes more effectively with RSSR for the deuterium atoms so that less of the RSSR is converted back to thiol.

To determine if the variation in RSSR yield ($\pm 5\%$) was great enough to affect the values of the $[HD]/[D_2]$ ratios, we performed the following experiment. A solution of *tert*-butyl mercaptan and 2,4-dimethylpentane was photolyzed for different times (0.5–2 hr), and the following ratios were measured: $[HD]/[D_2]$, $[H_2]/[D_2]$, and $[RSSR]/([RSD] + [RSSR])$. The disulfide yield increased from 2.5 to 9.9%. For the same solutions, however, $[HD]/[D_2]$ and $[H_2]/[D_2]$ remained constant at 2.01 ± 0.05 and 0.40 ± 0.01 , respectively. This proves that a change in a factor of four in the disulfide yield does not affect the ratios of the gaseous products nor the k_{HI}/k_2 ratios.

This last experiment also shows that reactions 5 and 6 are unimportant for 2,4-dimethylpentane. If reaction 5 is important in this kinetic scheme, then it can be seen that the $[HD]/[D_2]$ ratio will decrease with extent of conversion. This is seen not to be the case. Reaction 6, a potential source of H· and H₂ (*via* reactions 15–17), is also eliminated as being important for hydrocarbons since no increase in the amount of H₂ is noted at longer reaction times.

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(42) C. Walling and R. Rabinowitz (*J. Amer. Chem. Soc.*, **81**, 1137 (1959)), obtained similar results for RSH yields in the photolysis of RSSR in cumene. These results were interpreted as photosensitization of the RSSR decomposition by the cumene. This explanation is not likely in our work since we used aliphatic solvents.

(43) See ref 9 and references cited therein.