

Alternatively, when methanol is excluded and the methylation carried out in THF solution using diazomethane, everheptose (11) is cleaved to 4 and 2. It is not unlikely that diazomethane besides methylating the phenolic hydroxyl group causes (a) the opening of the ester linkage (which is probably enhanced by the hydrogen bonding with the β -hydroxyl group in the intermediate) and (b) cyclization to the δ -lactone 4 through anion formation.⁹

Acknowledgment. We wish to express our thanks to Sir Derek Barton and Professor J. Meinwald for many stimulating discussions.

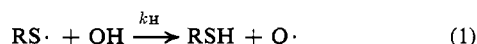
(9) Satisfactory elementary analyses were obtained for all new compounds; ir spectra were recorded in chloroform solution; optical rotations were measured in chloroform solution; nmr spectra were taken at 100 MHz in CDCl_3 with internal TMS standard. All the coupling constant values were obtained using spin-spin decoupling experiments. The mass spectral assignments were based on high resolution mass spectrometry.

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Received September 5, 1972

Hydrogen Abstraction by Thiyl Radicals

Sir:

Data are available on the selectivity and polar character of most common free radicals,¹ but the thiyl radical, a ubiquitous species in organic chemistry² and radiation biology,³ is a notable exception. Hydrogen abstraction by thiyl radicals from organic substrates (eq 1) is well documented.^{2a,d,4} However, a quantita-



tive study of this reaction has not been published, although work by Walling and Rabinowitz⁴ and by van Zwet and Kooyman^{5,6} has provided important semi-quantitative data. Kellogg, in a recent review,^{2a} has stated that it will be difficult to obtain quantitative data on reaction 1 because of its reversibility.

A method for the quantitative study of eq 1 is presented here; the method was conceived in order to take advantage of the very reversibility of eq 1 which has hindered previous studies. The key of this method is to utilize tritium-labeled thiol (RSH^*) as a solvent; in this milieu, $\text{Q}\cdot$ radicals generated in eq 1 abstract

(1) (a) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, Chapter 12; (b) W. A. Pryor, D. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972); (c) R. S. Davidson, *Quart. Rev., Chem. Soc.*, **21**, 249 (1967); (d) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 1 (1965); (e) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; (f) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(2) (a) R. M. Kellogg, "Methods in Free-Radical Chemistry," Vol. II, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, p 101; (b) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **9**, 273 (1970); (c) S. G. Cohen, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967; (d) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 602 (1964).

(3) (a) "Radiation Damage and Sulphydryl Compounds," International Atomic Energy Agency, Vienna, 1969; (b) K. I. Altman, G. B. Gerber, and S. Okada, "Radiation Biochemistry," Vol. I, Academic Press, New York, N. Y., 1970; (c) S. Colowick, *et al.*, Ed., "Glutathione," Academic Press, New York, N. Y., 1954.

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

(5) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **87**, 48 (1968).

(6) H. van Zwet and E. C. Kooyman, *ibid.*, **86**, 1143 (1967).

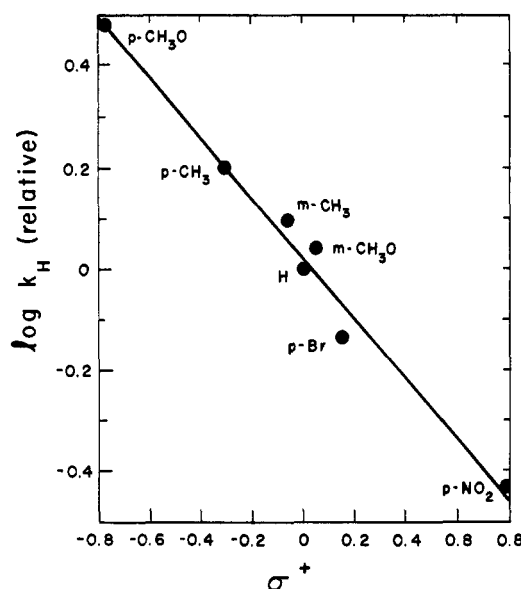
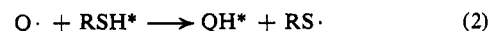


Figure 1. A plot of relative values of k_H (eq 1) vs. Hammett σ^+ constants.

hydrogen from RSH^* to re-form the substrate QH^* which is now tritium labeled (eq 2). The level of



radioactivity in the recovered QH^* can be related to the specific rate constant for eq 1. Tritium isotope effects are involved in the calculation, but they can be evaluated independently.^{7,8} Because there are no data in the literature with which to test our method, we have developed two kinetic schemes for the determination of relative values of k_H (eq 1).

Table I gives data on the cyclohexanethiyl radical.

Table I. Relative Rate Constants per Reactive Hydrogen for Hydrogen Abstraction by the Cyclohexanethiyl Radical at 80°^a

Hydrogen donor	n^b	Relative k_H^c	
		Scheme I	Scheme II
Anisole	3	<<0.032	
<i>m</i> -Xylene	6	0.043	0.048
Mesitylene	9	0.057	
<i>p</i> -Xylene	6	0.066	
<i>p</i> -Nitroethylbenzene	2	0.37	
<i>p</i> -Bromoethylbenzene	2	0.73	
Ethylbenzene	2	(1.0)	(1.0)
<i>m</i> -Ethylanisole	2	1.1	
<i>m</i> -Ethyltoluene	2	1.25 ^d	
<i>p</i> -Ethyltoluene	2	1.6 ^d	
<i>p</i> -Ethylanisole	2	3.0	
Diphenylmethane	2	1.5	
Cumene	1	6.3	6.6
<i>p</i> -Cymene	1	8.8	

^a These data have not been corrected for the ratio of isotope effects.^{7,13} ^b Number of reactive hydrogens assumed. ^c Reproducibility suggests these data are accurate to $\pm 5\%$. ^d k_H applies to secondary benzylic position.

A Hammett plot⁹ of the data for substituted ethylbenzenes at 80° gives an excellent correlation using σ^+ with

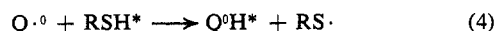
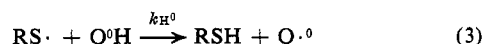
(7) W. A. Pryor and K. G. Kneipp, *J. Amer. Chem. Soc.*, **93**, 5584 (1971).

(8) E. S. Lewis and M. M. Butler, *Chem. Commun.*, 941 (1971).

(9) Substituent constants taken from J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

$\rho^+ = -0.59$ (correlation coefficient, $r = 0.997$) and a poorer correlation with σ ($\rho = -0.77$, $r = 0.944$).

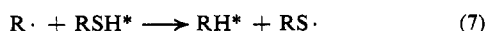
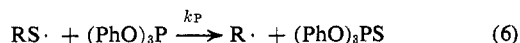
Our first scheme for determining k_H values involves thermal homolysis of AIBN in solvent RSH* containing two hydrogen donors, QH and Q⁰H. The radicals from the initiator convert a fraction of the thiol to thiyl radicals^{7,8,10-12} which abstract hydrogen from QH or Q⁰H (eq 1 and 3). The Q· and Q⁰· radicals



then undergo reactions 2 and 4 and become labeled. Kinetic analysis leads to eq 5, where A_{QH} and A_{Q^0H} are the molar specific activities of the recovered substrates and I and I^0 are the isotope effects k_H/k_T on eq 2 and 4, respectively.¹³

$$k_H/k_{H^0} = (I/I^0)(A_{QH}/A_{Q^0H}) \quad (5)$$

In the second scheme, triphenyl phosphite (TPP) replaces one of the hydrogen donors.¹⁴



Kinetic analysis yields eq 8, where A_{RSH} is the molar

$$A_{QH}[TPP] = (k_H/k_P)(I^{-1})(A_{RSH})[RH] \quad (8)$$

specific activity of the thiol and $[RH]$ is the total yield of cyclohexane. A plot of $A_{QH}[TPP]$ vs. $[RH]$ at constant thiol activity yields a straight line with zero intercept and a slope which is proportional to k_H . Data from such plots for two substrates yield relative k_H values (eq 9).

$$k_H/k_{H^0} = (I/I^0)(\text{slope for QH plot})/(\text{slope for Q}^0\text{H plot}) \quad (9)$$

The assumptions made in deriving the kinetic expressions, eq 5 and 9, are as follows. (1) $[RSH] \gg [RST]$. (2) Only a small fraction of the QH becomes labeled. Both requirements 1 and 2 were satisfied in our work. (3) A steady state in the concentration of Q· radicals obtains. (4) Only the listed reactions are involved in the formation of the products studied. This was demonstrated by showing that extensive variation in the reaction variables (including replacing AIBN by *tert*-butyl peroxy-cyclohexanecarboxylate) does not affect the relative values of k_H .

Controls also were performed in which the value of $(k_H)_A/(k_H)_B$ obtained from direct competition between substrates A and B was compared with the results of two separate cross-competitions, one involving A and C (a third substrate) and another between B and C. These direct and indirect measures of $(k_H)_A/(k_H)_B$ always were in good agreement.

(5) Q· and Q⁰· radicals are not involved in termination processes. This was verified for cumyl radicals

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(11) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *ibid.*, **76**, 180 (1957).

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(13) The ratio of the isotope effects for relatively stable Q· radicals as used here will be quite close to unity.⁷

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by detailed product studies using glpc of reaction mixtures similar to those from scheme I in Table I but containing cumene as the only hydrogen donor. The amounts of C₆H₁₁SC(CH₃)₂Ph, C₆H₁₁SCH₂CH(CH₃)Ph, and bicumyl account for less than 1% of the cumyl radicals formed in a sample. The data also show that the yield of isobutyronitrile was twice that of dicyclohexyl disulfide, indicating that dimerization of the thiyl radicals is the only significant termination reaction occurring in these systems.

Our ρ^+ value of -0.59 can be compared with $\rho^+ = -0.86$ obtained for abstraction by atomic bromine,¹⁵ and $\rho^+ = -0.53$ for abstraction by trichloromethyl radicals¹⁶ (all three ρ values apply to ethylbenzenes at 80°).^{16,17} These three ρ values are of interest in the light of the recent novel and ingenious suggestions of Zavitsas.¹⁸⁻²⁰

Acknowledgments. This research was partially supported by National Institutes of Health Grant 11908. One of us (G. G.) thanks the Consejo Nacional de Ciencia y Tecnología (Mexico) for a scholarship.

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(16) The ρ^+ values for bromine atoms and trichloromethyl radicals toward toluenes are -1.39 (80°; C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963)) and -1.46 (50°; E. S. Huyser, *ibid.*, **82**, 394 (1960)), respectively.

(17) The original data on addition of thiyl radicals to olefins (see ref 1 pp 216-218) indicated a substantial electrophilic polar character for the radicals. The newer, revised data, however, suggest a much smaller effect, perhaps, as suggested by Kellogg, because the reactions are appreciably exothermic (ref 2a, pp 39-41).

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Received September 6, 1972

Photo-CIDNP Detection of Transient Intermediates. The Enol of Acetophenone

Sir:

CIDNP studies are ideally suited to reveal the presence of thermally unstable products of radical reactions.¹ The large intensity enhancements in CIDNP spectra result from polarization in newly formed product molecules (and decay with T₁) so that, unlike most physical techniques, it is the concentration of recently formed species, rather than the total concentration of the species, that is important. We now report an example of this CIDNP application in the detection of the enol formed during the photolysis of acetophenone.

Hydrogen abstraction reactions of the triplet excited state of acetophenone (1) have long been known to lead to reductive dimerization of the ketone.² Recently,³ a novel hydrogen abstraction from phenol (2) by acetophenone was reported to lead to 1,2-dibenzoylthane (3) as well as acetophenone pinacol in high yield. The

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