BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (1), 317—318 (1977)

Absolute Rate Constants for Hydrogen Abstraction from Some Aromatic Hydrocarbons by *p*-Chlorophenylthiyl Radical

Tokuji Miyashita, Masashi Iino, and Minoru Matsuda
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980

(Received June 25, 1976)

Synopsis. The absolute rate constants for hydrogen abstraction from cumene, *p*-cymene, and tetralin by *p*-chlorophenylthiyl radical have been determined by means of flash-photolysis and kinetic absorption spectrophotometry. The results are discussed in comparison with those reported for other types of free radicals.

Thiyl radical can abstract hydrogen atom from hydrocarbons[1,2] containing reactive hydrogen atom and also from compounds containing functional groups such as aldehyde and alcohol.[1] However, few kinetic studies on these reactions have been carried out because of the difficulty of elimination of the reverse reaction under the usual steady state reaction conditions:

$$\mathrm{RS}\cdot + \mathrm{R'H} \underset{k_{-\mathrm{H}}}{\overset{k_{\mathrm{H}}}{\rightleftarrows}} \mathrm{RSH} + \mathrm{R'}\cdot \tag{1}$$

This difficulty has been overcome by using tritium-labeled thiol as a solvent[2] for obtaining the relative rate constants for hydrogen abstraction in the case of the cyclohexylthiyl radical.

We have determined the absolute rate constants for hydrogen abstraction from some hydrocarbons by *p*-chlorophenylthiyl radical by following the decay of a short-lived and a very small amount of the free thiyl radical by means of flash-photolysis and kinetic absorption spectrophotometry;[3] this can effectively eliminate such a reverse reaction. The flash apparatus delivered a flash with an energy of 125 J from xenon-filled lamps. The flash exhibited a half-peak duration of 10 μs.

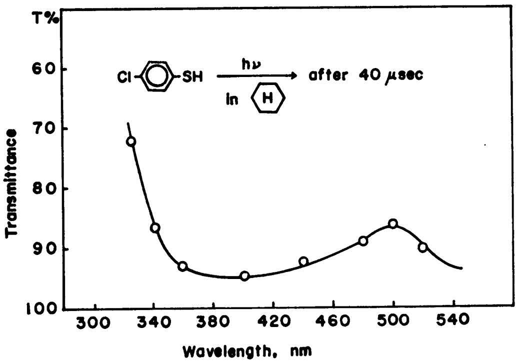

Fig. 1. Electronic spectrum of *p*-chlorophenylthiyl radical produced by flash photolysis of *p*-chlorophenylthiol.

Figure 1 shows the absorption spectrum of *p*-chlorophenylthiyl radical in cyclohexane recorded after 40 μs of the flash. The same spectrum has been reported by Thyrion,[4] and Tagami *et al.*[5] The decay of the *p*-chlorophenylthiyl radical has been followed by monitoring the absorbance at 500 nm. The behavior of the decay observed for *p*-chlorophenylthiyl radical in solutions can be divided into the following three patterns. (a) In cyclohexane and toluene solutions the thiyl radical decays according to second-order kinetics, indicating the occurrence of recombination of the thiyl radical in both the solvents:

$$2\mathrm{RS}\cdot \xrightarrow{k_t} \mathrm{RS{-}SR} \tag{2}$$

Table 1. Decay kinetics of *p*-chlorophenylthiyl radical in various hydrocarbons (23 °C)

Solvent	Decay order	Rate constant ($\mathrm{l\ mol^{-1}\ s^{-1}}$)
Cyclohexane	2 nd	$2k_t/\varepsilon = 4.1 \times 10^6$ [a]
		$2k_t = 1.4 \times 10^9$ [a]
Cyclohexane	2 nd	$2k_t/\varepsilon = 4.1 \times 10^6$
		$2k_t = 1.2 \times 10^9$ [b]
Toluene	2 nd	$2k_t/\varepsilon = 4.8 \times 10^6$
		$2k_t = 1.4 \times 10^9$ [b]
Ethylbenzene	2 nd—1 st	—
Tetralin	1 st	$k_{\mathrm{H}} = 1.50 \times 10^2$
Cumene	1 st	$k_{\mathrm{H}} = 1.20 \times 10^3$
p-Cymene	1 st	$k_{\mathrm{H}} = 1.42 \times 10^3$

a) Ref. 4, the rate constant for the phenylthiyl radical. b) Calculated by using the reported ε[5] (280 dm³/mol cm at 510 nm) for the *p*-chlorophenylthiyl radical.

The relevant second-order rate constants determined are given in Table 1. A similar recombination rate constant was reported for phenylthiyl radical in cyclohexane[4] (Table 1). (b) The decay in large excess of tetralin, cumene, and *p*-cymene, obeys pseudo first-order kinetics. (c) In the ethylbenzene solution, competitive reactions between the pseudo first-order reaction (hydrogen abstraction from the solvent, the forward reaction in Eq. 1) and recombination take place. The pseudo first-order rate constants were reduced to absolute second-order rate constants per reactive hydrogen atom. These results are also given in Table 1.

Ingold gave the absolute rate constants for hydrogen

Table 2. Absolute rate constants for hydrogen abstraction from cumene by short-lived radicals

Radical	Absolute rate constant k_{H} ($\mathrm{l\ mol^{-1}\ s^{-1}}$)
$\mathrm{OH}\cdot$	Diffusion controlled[a]
$\mathrm{Br}\cdot$	1.2×10^7 (40 °C)[a]
$\mathrm{C_6H_5}\cdot$	$\simeq 10^7$ (60 °C)[a]
$t\text{-}\mathrm{C_4H_9O}\cdot$	4.3×10^4 (40 °C)[a]
$p\text{-}\mathrm{ClC_6H_4S}\cdot$	1.2×10^3 (23 °C)[b]
$\mathrm{Cl_3C}\cdot$	1.3×10^2 (40 °C)[a]
$t\text{-}\mathrm{C_4H_9OO}\cdot$	3.3×10^{-1} (30 °C)[a]
$-\mathrm{CH_2(C_6H_5)CH}\cdot$ [c]	1.3×10^{-3} (60 °C)[a]

a) Ref. 6. b) This work. c) Polystyryl radical.

abstraction by a variety of radicals.[6] These absolute rate constants for α-hydrogen atom abstraction from cumene by various types of free radicals are summarized together with ours in Table 2. We see that the *p*-chlorophenylthiyl radical abstracts about 30 times faster than the trichloromethyl radical, and about 20 times slower than the *t*-butoxyl radical at 23 °C. Activation energies[6] of 6 kcal/mol and 12 kcal/mol, in the abstraction of *t*-butoxyl and trichloromethyl radicals, respectively, from toluene, were used in the calculation of the rate constants at 23 °C. Zwet and Kooyman reported that the triphenylmethylthiyl radical is more reactive in hydrogen abstraction reactions than the trichloromethyl radical, but less reactive than the *t*-butoxyl radical or chlorine atom.[8] Their findings agree with ours. The slightly greater reactivity toward *p*-cymene than cumene (Table 1) is reasonable in the light of electrophilicity of the thiyl radicals.[2,7]

The authors wish to thank Asst. Prof. Dr. H. Kokubun and Dr. K. Kikuchi, Tohoku University, for their introduction to flash photolysis technique and for the use of the apparatus.

References

1) R. M. Kellogg, "Methods in Free-Radical Chemistry," Vol. II, ed by E. S. Huyser, Marcel Dekker, New York (1969), p. 101.

2) W. A. Pryor, G. Gojon, and J. P. Stanley, *J. Am. Chem. Soc.*, **95**, 945 (1973).

3) G. Porter, "Technique of Organic Chemistry," Vol. VIII, Part 2, ed by A. Weissberger, Interscience Publishers, New York (1963), p. 1055.

4) F. C. Thyrion, *J. Phys. Chem.*, **77**, 1478 (1973).

5) M. Tagami, T. Takakura, M. Okuyama, and H. Kamata, 8th Symposium on High Speed Reactions, 1973, p. 45.

6) K. U. Ingold, "Free Radicals," Vol. I, ed by J. K. Kochi, John Wiley & Sons, New York (1973), p. 74.

7) C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 2559 (1948).

8) Ref. 1, p. 104.