The Relative Reactivities of Different C–H Bonds in the Photochemical Sulfoxidation of *n*-Hexane[1]

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(Received April 30, 1965)

The present authors have previously postulated,[2] in the photochemical sulfoxidation of *n*-hexane, a mechanism involving the simultaneous steps of a chain reaction via persulfonate radical and a molecular mechanism via excited sulfur trioxide; the primary process in the radical chain seems to involve two simultaneous processes, i. e., energy transfer and hydrogen abstraction with excited sulfur dioxide.

The relative reactivities of different C–H bonds in *n*-heptane towards ultraviolet light-excited sulfur dioxide have recently been estimated by Asinger, Fell and Pöttkamper.[3] In order to estimate the relative reactivities, the heptanesulfonic acids produced were converted to the corresponding methyl heptanesulfonates, which had been determined by gas chromatography.

The present paper will describe the results obtained in a study of the relative reactivities of different C–H bonds towards excited sulfur dioxide and sulfur trioxide in the photochemical sulfoxidation of *n*-hexane, together with the results of the comparison of these data with those of the photochemical chlorination.

Experimental

Materials.—*n*-Hexane was purified by a previously reported procedure.[2] Acetic anhydride, dichloromethane, sulfur dioxide and oxygen were of commercial materials of an extra pure grade. Thionyl chloride (b. p. 78—79°C) and dimethyl formamide (b. p. 75—77°C/63 mmHg) were purified by the fractionation of commercial materials of an extra pure grade. Authentic 2-hexanesulfonyl chloride was prepared as follows: 2-hexanol (b. p. 79—80°C/81 mmHg; n_D^{25} 1.4133 (lit.[4] n_D^{25} 1.4136); its 3,5-dinitrobenzoate, m. p. 37.8—38.5°C (lit.[5] m. p. 38°C)) was prepared by Grignard synthesis from *n*-butyl bromide and acetaldehyde; it was converted by phosphorous tribromide to 2-hexyl bromide, which was then converted to 2-hexanesulfonyl chloride (b. p. 60—62°C/4.5 mmHg; n_D^{25} 1.4630 (lit.[6] n_D^{25} 1.4610)) via 2-hexyl thiocyanate.[7,8] Authentic 1-hexanesulfonyl chloride (b. p. 92—93°C/4 mmHg; n_D^{25} 1.4612 (lit.[9] n_D^{25} 1.4563)) and 3-hexanesulfonyl chloride (b. p. 64°C/5.5 mmHg; n_D^{25} 1.4637) were similarly prepared from 1-hexanol (b. p. 156—157°C) and 3-hexanol (b. p. 134—135°C; n_D^{25} 1.4134 (lit.[10] n_D^{25} 1.4139); its 3,5-dinitrobenzoate, m. p. 75.2—75.5°C (lit.[5] m. p. 77°C)) respectively. The purities of all the alcohols, bromides, thiocyanates and sulfonylchlorides examined were confirmed by gas chromatography.

The Sulfoxidation of *n*-Hexane.—Sulfur dioxide (0.5—2 l./hr.) and oxygen (0.3—2 l./hr.) were introduced simultaneously into a mixture of *n*-hexane (0.3 mol., 40 ml.) and acetic anhydride (0.016 mol.) under ultraviolet light (Toshiba SHL-100 UV) at 1—28°C for 1 hr. After irradiation had ended, treatment in a way similar to that described in a previous paper[2] gave sodium hexanemonosulfonates.

The Conversion of Sodium Hexanesulfonates to Their Sulfonyl Chlorides.—The procedure employed was similar to that reported by Kirkland.[11] A mixture of the resulting sodium hexanesulfonates

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1) Contribution No. 73. Presented in part at the 3rd Symposium on Oil Chemistry, Nagoya, November, 1964.

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3) F. Asinger, B. Fell and S. Pöttkamper, *Chem. Ber.*, **97**, 3092 (1964).

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11) K. Kirkland, *Anal. Chem.*, **32**, 1388 (1960).

(1.5 g.) and fresh thionyl chloride (50 ml.) in the presence of dimethyl formamide (1.5 ml.) was refluxed until the evolution of sulfur dioxide had subsided (1—2 hr.); then it was cooled. Dichloromethane (about 50 ml.) was added to the reaction product, and the precipitate of sodium chloride was filtered off. The unreacted thionyl chloride and the solvent were carefully removed by evaporation under moderately reduced pressure, and dichloromethane (3—5 ml.) was added to the remaining sulfonyl chloride. The isomeric hexanesulfonyl chloride content of the solution was determined by gas chromatography.

The Determination of the Isomeric Hexanesulfonyl Chlorides by Gas Chromatography.—The vapor-phase chromatographic determination of the isomers was carried out using a 5 m. column (diameter 4 mm.) containing polyethylene glycol 4000 (1% by weight)/C-22 (40—60 mesh), and with helium as a carrier gas (54 ml./min.) at 130°C (Fig. 1); the similarity of the retention times of the peaks of the authentic material to those of the peaks of the sample established their identity. The molar ratio of the isomers was calculated by means of the paper-peak-weight ratio. No appreciable decomposition of hexanesulfonyl chlorides to the corresponding hexyl chlorides was observed under these conditions.

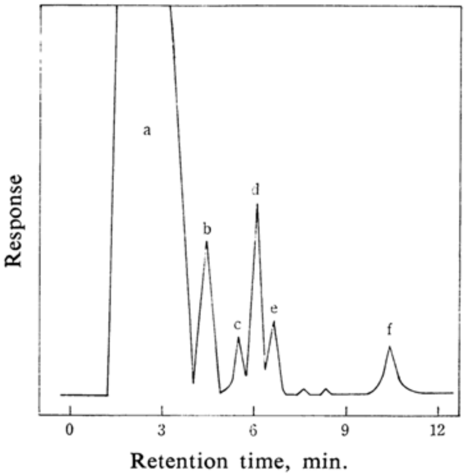

Fig. 1. Typical chromatogram of 1-, 2- and 3-hexanesulfonyl chlorides.
a: Dichloromethane, b: Dimethylformamide, c: Unknown, d: 3-Hexanesulfonyl chloride, e: 2-Hexanesulfonyl chloride and f: 1-Hexanesulfonyl chloride.

The Photochlorination of *n*-Hexane.—Chlorine (0.3—0.5 l./hr.) was introduced into *n*-hexane (0.3 mol., 40 ml.) under ultraviolet light at −10—+28°C for 1 hr. After the irradiation had ended, nitrogen was bubbled into the reaction mixture in order to remove the free chlorine and hydrogen chloride in the mixture. The resulting solution was washed with 1 N aqueous sodium hydrogen carbonate and then with water, and dried with sodium sulfate. The isomeric hexyl monochloride content was determined by gas chromatography, using a column similar to that used for hexanesulfonyl chloride at 37°C. The hexyl monochloride content as a whole in the resulting chlorinated hexane was about 83%.

Results and Discussion

The sodium 1-, 2- and 3-hexanesulfonates obtained by the sulfoxidation of *n*-hexane were converted to the corresponding sulfonyl chlorides, and then the latter were estimated by gas chromatography. The relative reactivity (R) of different C–H bonds towards excited SO_2 and SO_3 is given by:

$$R=\left(\frac{\text{Mol.\% of the isomer in the product}}{\left(\begin{array}{l}\text{Total number of C–H bonds at the}\\ \text{corresponding position}\end{array}\right)}\right)\Big/R_1$$

where

$$R_1=\frac{\text{Mol.\% of 1-isomer}}{\text{Total No. of C–H bonds at the 1-position}}$$

Table I summarizes the relative reactivities of different C–H bonds in the photochemical sulfoxidation and chlorination of the *n*-hexane in our hands, together with the results in the literature. As Table I shows, the relative reactivity, 2.1—3.6, for the secondary vs. the primary C–H bond of *n*-hexane approximates those in the photochemical sulfoxidation[12)] and sulfochlorination[13)] of *n*-dodecane and the photochlorination of *n*-heptane[14)] and *n*-dodecane.[15,16)] In contrast, it has recently been reported[3)] that the relative reactivity for C(secondary) vs. C_1 in the photochemical sulfoxidation of *n*-heptane without acetic anhydride is about 30, although this value is very different from those obtained in photochemical reactions by other workers. At any rate, the increase in the relative reactivity of C(secondary) may be accounted for by the stability of the secondary carbon radical being greater than that of the primary radical.

On the other hand, since it may be expected that the C_3–H bond is more sterically hindered, it is surprising to observe that the reactivity of the C_2–H bond is lower than that of the C_3–H bond. This fact may be explained by assuming temporarily the tentative formation of a six-membered ring[17,18)] of the 2-hexyl radical, which results in the inhibition of the approach of SO_2 or SO_3 to the 2-position, thus

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TABLE I. RELATIVE REACTIVITIES OF C–H BONDS FOR TYPICAL PHOTOCHEMICAL REACTIONS OF *n*-ALKANES

Reaction	Substrate	Temp. °C	Relative reactivity			
			C_1–H	C_2–H	C_n–H	2_{ry}C–H/1_{ry}C–H
Chlorination	*n*-Hexane	−7—28	1	2.9—3.5	3.0—3.8 (*n*=3)	3.1—3.6
	n-Heptane[14]	98	1	3.4[a]	3.3(*n*=3)[a] 3.3(*n*=4)[a]	2.4[a]
	n-Dodecane[15]	20	1	5.8[a]	6.9[a] (*n*=3—6)	6.7[a]
Sulfo-chlorination	*n*-Dodecane[13]	25	1	1.6[a]	3.8[a] (*n*=3—6)	3.3
Sulfoxidation	*n*-Hexane	1—28	1	0.8—1.3	3.2—6.2 (*n*=3)	2.1—3.6
	n-Heptane[3]	20	1	32[a]	29(*n*=3)[a] 27(*n*=4)[a]	30
	n-Dodecane[12]	30—80	1	3.1[a]	5.7[a] (*n*=3—6)	3.3

a) Calculated values based on the experimental data in the literature.[3,12–15]

TABLE II. EFFECT OF THE RATIO $[SO_2]/[O_2]$ ON THE RELATIVE REACTIVITIES OF C–H BONDS ($[n\text{-}C_6H_{14}]/[Ac_2O]$: 19; Irradiation time: 1 hr.)

$[SO_2]/[O_2]$	Temp. °C	Relative reactivity			
		C_1–H	C_2–H	C_3–H	2_{ry}C–H/1_{ry}C–H
0.5	18—19	1	0.8	4.0	2.4
2	11—18	1	1	3.3	2.2
10	18—19	1	0.9	6.2	3.6

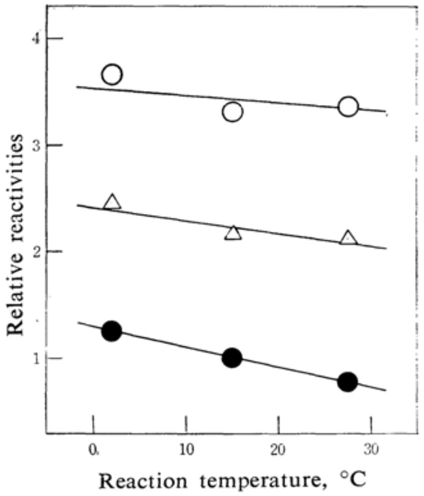

Fig. 2. Temperature dependence of the relative reactivities in photochemical sulfoxidation of *n*-hexane.
●: C_2–H, ○: C_3–H
△: (Secondary C–H)/(Primary C–H)

lowering the reactivity of C_2–H bonds compared with that of C_3–H bonds. This assumption may also explain the fact that the temperature dependence of the reactivity of C_2–H bonds is somewhat greater than that of C_3–H bonds (Fig. 2), for rings are formed more easily at a higher temperature. Since the C–H bond length is short, the five-membered ring from the 3-hexyl radical may approach the four-membered ring, which is less stabilized. Although the temperature effect on the reactivity is small in the 0—30°C range, an increase in the temperature results in a small decrease in the reactivity for photochemical sulfonates by sulfur trioxide, as is shown in Fig. 2. Furthermore, the ratio of SO_2 vs. O_2 also affects the relative reactivity, particularly for C_3–H bonds (Table II).

Table III shows the findings on the photochemical chlorination of *n*-hexane, where such steric hindrance of the six-membered ring seems to be small. In this case, the difference in the relative reactivities of C_2–H and C_3–H bonds is small. Such a difference in the behavior of chlorine and sulfur dioxide has been reported in the photochemical chlorination of

TABLE III. RELATIVE REACTIVITIES OF C–H BONDS IN THE PHOTOCHLORINATION OF *n*-HEXANE (Flow rate of Cl_2: 0.3—0.5 l./hr.; Irradiation Time: 1 hr.)

Temp. °C	Relative reactivity		
	C_1–H	C_2–H	C_3–H
−7—−5	1	3.5	3.0
21—22	1	2.9	3.2
27—28	1	3.4	3.8

isobutane, giving *t*-butyl chloride,[19] and the sulfochlorination of the same substrate, giving isobutanesulfonyl chloride alone.[20]

Summary

The product mixture of isomeric hexanesulfonic acids in the ultraviolet light-induced sulfoxidation of *n*-hexane under various conditions has been analyzed by gas chromatography. On the basis of the data thus obtained, the relative reactivities of different C–H bonds in *n*-hexane towards light-excited sulfur dioxide and sulfur trioxide have been estimated. The ratio of the reactivities of C_1–H : C_2–H : C_3–H has been calculated to be 1 : 0.8—1.3 : 3.2—6.2. The higher reaction temperatures tend to lower the reactivity of C_2–H. The mole ratio of SO_2 vs. O_2 has an appreciable effect on the composition of the isomers. The lower reactivity of C_2–H than that of C_3–H may be explained by the intermediary formation of a six-membered ring.

The authors are grateful to the Seitetsu Chemical Co. for their gift of sulfur dioxide.

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