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THE PHOTOCHEMICAL SULPHOXIDATION OF *n*-HEXANE[1]

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Abstract—The photochemical sulphoxidation of *n*-hexane in the presence of acetic anhydride giving hexanesulphonic acid has been examined. A maximum yield of 26% is obtained when the sulphoxidation is carried out with a molar ratio of *n*-hexane : acetic anhydride of 19 : 1. An increase in the reaction temperature to 28° serves to increase the yield, and for *n*-decane the limit is reached at about 80°. The reaction is sensitized with acetophenone or *p*-chloroacetophenone, while it is inhibited by 2,3-dimethylbutane or 1-hexene. Mechanisms involving simultaneous steps of chain reaction via persulphonate radical and a molecular mechanism via excited sulphur trioxide are discussed. The photochemical primary process in the radical chain seems to involve two simultaneous processes, i.e., the energy transfer from excited sulphur dioxide to substrate followed by the homolytic C—H bond fission on one hand, and the formation of alkyl radicals by the abstraction of hydrogen with excited sulphur dioxide on the other.

THE light-induced reaction of alkanes or cycloalkanes with a mixture of sulphur dioxide and oxygen forming sulphonic acid has been called "sulphoxidation." The mechanism involving a radical chain via persulphonic acid has been postulated by Orthner,[2] Graf[3] and Asinger.[4] The gamma initiated sulphoxidation[5–7] is also a radical chain reaction.

Alternatively, Topchiev *et al.* suggested a non-chain mechanism via sulphinic acid on the basis of their doubt of the light-induced initiation.[8]

The present paper describes results of an investigation on the light-induced sulphoxidation of *n*-hexane, *n*-decane and hexyl chloride including the effect of conditions on the yield, the sensitization with aromatic ketones, and the inhibition with isoalkane or olefin.

RESULTS AND DISCUSSION

The effect of reaction conditions on the yield of sulphonic acid

Although the solubility of sulphur dioxide in *n*-hexane decreases with temperature (Fig. 1), the yield of sulphonic acid increases with temperature as shown in Fig. 2. The temperature effect may be explained by the acceleration of the radical formation

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[1] Contribution No. 68. Presented in part at the Annual Meeting of Japan Oil Chemists' Society, Nagoya, November, 1963 and at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[2] L. Orthner, *Angew. Chem.* **62**, 302 (1950).

[3] R. Graf, *Liebigs Ann.* **578**, 50 (1952).

[4] F. Asinger, G. Geiseler and H. Eckoldt, *Chem. Ber.* **89**, 1037 (1956).

[5] J. F. Black and E. F. Baxter, Jr., *Soap Chem. Specialties* **34** (10), 43 (1958).

[6] R. V. Dzhagatspanyan, V. I. Zetkin and E. N. Zykova, *Chem. Abstr.* **58**, 4074 (1963).

[7] O. D. Hummel, M. Werner and C. Schneider, *Liebigs Ann.* **673**, 13 (1964).

[8] A. V. Topchiev, G. H. Tsiguro and G. V. Gryanznov, *Dokl. Akad. Nauk USSR* **113**, 1302 (1957); *Chem. Abstr.* **51**, 16111 (1957).

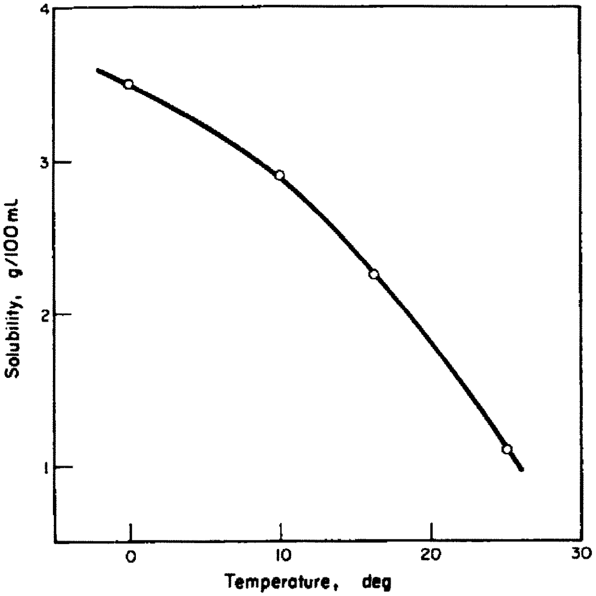

FIG. 1. Solubilities of sulphur dioxide in n-hexane.

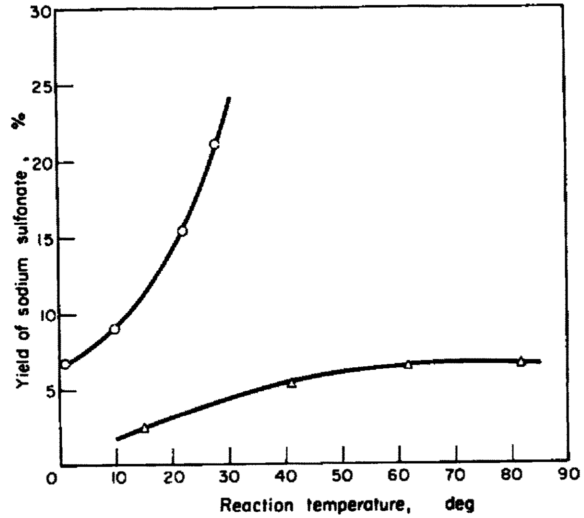

FIG. 2. The effect of reaction temperature on the yield SO_2/O_2: 2, irradiation time: 1
○: n-hexane, [n-hexane]/[acetic anhydride] = 37
△: n-decane, [n-decane]/[acetic anhydride] = 19.

by the decomposition of acetyl hexanesulphonyl peroxide or reaction of excited sulphur dioxide with hydrocarbon and also by the promotion of the propagation reaction. The poor yield may be due to an inefficient primary act[9] and/or to the termination by coupling of radicals.

As shown in Fig. 3, the yield increases with increasing molar ratio of acetic anhydride to *n*-hexane to a maximum and then decreases. An increase in yield can be

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[9] M. K. Phibbs and B. Deb. Daswent, *J. Chem. Phys.* **18**, 679 (1950).

explained by an increase in the concentration of acetyl sulphonyl peroxide which dissociates to form new chain carriers as follows;

$$RSO_2O_2H + (CH_3CO)_2O \rightarrow RSO_2O_2COCH_3 + CH_3COOH$$
$$RSO_2O_2COCH_3 \rightarrow RSO_2O\cdot + \cdot OCOCH_3$$
$$RSO_2O\cdot + RH \rightarrow RSO_3H + R\cdot$$
$$CH_3COO\cdot + RH \rightarrow CH_3COOH + R\cdot$$

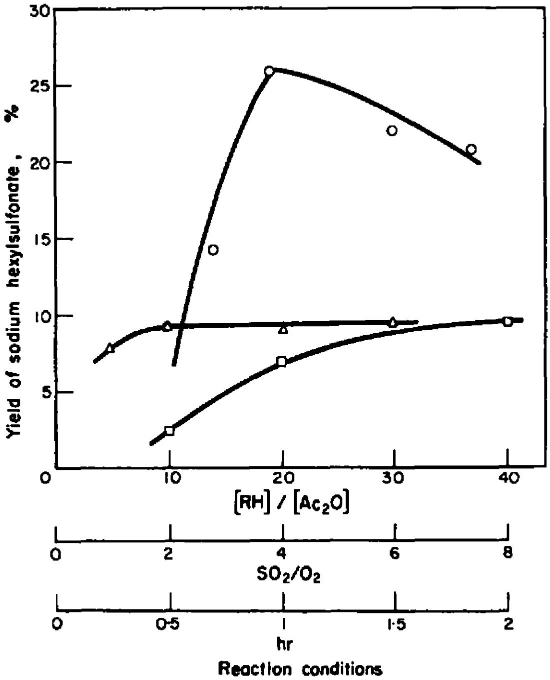

Fig. 3. The effect of reaction conditions on the yield

○: RH/Ac_2O (mole ratio) (SO_2/O_2 = 2, reaction temperature = 25–28, irradiation time = 1 hr)

△: SO_2/O_2 (mole ratio) (reaction temperature = 9–11, irradiation time = 1 hr, RH/Ac_2O = 37)

□: irradiation time (hr) (SO_2/O_2 = 2, reaction temperature = 18–19, RH/Ac_2O = 37).

Inhibition of photochemical sulphoxidation

It has been reported that the addition of 2,3-dimethylbutane or 1-hexene reduces the yield in the gamma sulphoxidation of *n*-hexane.[5] The inhibition was also observed during photochemical sulphoxidation, i.e., the addition of 1 vol% 1-hexene or 2,3-dimethylbutane lowers the yield based on *n*-hexane to 9·1 or 6·9%, respectively (Fig. 4).

The inhibitory action of 1-hexene may be caused by the formation of allyl radicals stabilized by the following resonance.

$$C{-}C{-}C{-}\underset{\cdot}{C}{-}C{=}C \leftrightarrow C{-}C{-}C{-}C{=}C{-}\underset{\cdot}{C}$$

Therefore, the activation energy for the abstraction of allyl secondary hydrogen may be smaller than that of simple primary hydrogen (ca. 750 cal/mole[10]) and secondary

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[10] J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.* **55**, 937 (1959).

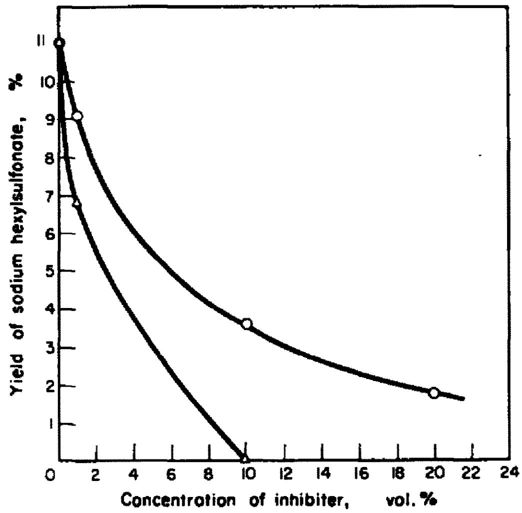

FIG. 4. Inhibition of photochemical sulphoxidation with 1-hexene (○) or 2,3-dimethylbutane (△).

hydrogen (ca. 450 cal/mole[10]) as a result of the resonance, and hence the allyl radical is formed more easily from 1-hexene. However, the resulting allyl radical is too stable to propagate the chain reaction.

The inhibition with 2,3-dimethylbutane is similarly explained by the easier formation of stable tertiary carbon radicals.

Photosensitization with aromatic ketones

In the photochemical reaction of benzophenone in isopropanol, the photoexcitation of a benzophenone molecule to a metastable triplet state results in the abstraction of an hydrogen atom from the alcohol, yielding a semibenzopinacol and a semipinacol radical.[11]

$$(C_6H_5)_2CO \xrightarrow{h\nu} (C_6H_5)_2CO^* \qquad (1)$$

$$(C_6H_5)_2CO^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH \qquad (2)$$

These radicals may be destroyed in the presence of oxygen to the original benzophenone, acetone and hydrogen peroxide.

$$(C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH + O_2 \rightarrow (C_6H_5)_2CO + (CH_3)_2CO + H_2O_2 \qquad (3)$$

Similarly, excited benzophenone may abstract an hydrogen atom from the hydrocarbon.[12]

$$(C_6H_5)_2CO^* + RH \rightarrow (C_6H_5)_2\dot{C}OH + R\cdot \qquad (2')$$

These reactions 3 and 2′ suggest that aromatic ketones behave as photosensitizers in this sulphoxidation.

The photosensitizer effect of five aromatic ketones is tabulated in Table 1, which lists the relative apparent induction period, i.e., the ratio of induction periods in the presence and absence of ketones. The period was estimated by the time required for

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[11] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Amer. Chem. Soc.* **81**, 1068 (1959).

[12] A. Charlesby, C. S. Grace and F. B. Pilkington, *Proc. Roy. Soc.* Ser. **A268**, 205 (1962).

insoluble acetyl hexanesulphonyl peroxide and/or hexanesulphonic acid to appear the solution becoming turbid owing to Tyndall phenomena. The value of *Y* represents the ratio (%) of the yield of sodium hexanesulphonate as compared with that in the absence of ketones. Here, the low value of *I* and high value of *Y* mean the effective sensitization as exemplified with acetophenone or *p*-chloroacetophenone in Table 1. In contrast, benzophenone or *p*-methylacetophenone possess an inhibitory action under these conditions. Thus a decrease of *I* on addition of *p*-methylacetophenone may be due to the action as "inner filter" and/or deactivator of SO_2^*. However, no reasonable explanation is conceivable for the observed negative result given by benzophenone.

TABLE 1. PHOTOSENSITIZATION WITH KETONES IN SULPHOXIDATION OF *n*-HEXANE AT 16–18°

(Relative apparent induction period I^a and relative yield^b)

		Mole ratio of ketone to *n*-hexane			
		1/100		1/20	
Ketone	λ_{max} (log ε)^c	*I*	*Y*	*I*	*Y*
None	—	1	100	1	100
Benzophenone	346 (2·08)	2	46	—	—
Acetophenone	320 (1·83)	1	92	0·6	92
p-Chloroacetophenone	318 (1·83)	0·5	92	1·7	92
Isobutyrophenone	320 (1·7)	0·7	69	1·2	—
p-Methylacetophenone	285 (2·70)	1·7	62	—	—

[a] Ratio of induction periods in the presence and absence of ketones.

[b] Ratio (%) of the yields of sodium hexanesulphonate in the absence and presence of ketones.

[c] Longest λ_{max} (mμ) in hydrocarbon.

The results obtained reveal a correlation between the photosensitizer effect of ketones and the stability of the corresponding $>\dot{C}OH$ radicals, i.e., the stability of radicals may be in the following order:

$$C_6H_5\underset{\bullet}{C}(OH)C_6H_5 > p\text{-}ClC_6H_4\underset{\bullet}{C}(OH)CH_3,\ C_6H_5\underset{\bullet}{C}(OH)CH_3 > C_6H_5\underset{\bullet}{C}(OH)C_3H_7.$$

Mechanisms of photochemical sulphoxidation

As shown in Table 2, the UV spectrum of sulphur dioxide in *n*-hexane shows a maximum at 290 mμ.

Since the reaction vessel was made of pyrex glass, the wave length of light below 300 mμ was almost eliminated during the sulphoxidation. If the sulphur dioxide molecule is excited by the absorption of light of 300 mμ, its excitation energy should be about 95 kcal/mole. This value is sufficient for cleavage of the C—H bond, since the bond strength is 94–102 kcal/g bond. Hence, the energy of excited sulphur dioxide may be transferred to the hydrocarbon molecule and then used for its decomposition to alkyl radical and hydrogen, which constitutes the primary process. The elimination of irradiation below 350 mμ with a filter (Toshiba Filter UV-35) results in

TABLE 2. ULTRAVIOLET ABSORPTION SPECTRA OF SULPHUR DIOXIDE AND SULPHUR TRIOXIDE

Solvent		λ_{max} (mμ) A-Band	λ_{max} (mμ) B-Band
SO_2	n-Hexane	—	290 [290 (ε = 250)[a]]
	Ethanol	218	278 (276[b])
		$\pi \rightarrow \pi^*$ transition	$n \rightarrow \pi^*$ transition
SO_3[c]	n-Hexane	—	290

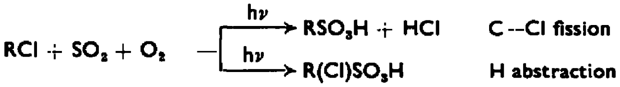
[a] H. Ley and E. König, *Z. physik. Chem.* **B41**, 365 (1938).

[b] K. Schaefer, *Z. Anorg. Chem.* **104**, 212 (1918).

[c] Commercial liquid sulphur trioxide (γ form).

a ca. 50% lower (but not null) yield of the sulphonic acid. This indicates that the primary process may simultaneously involve, in addition to the energy transfer described, hydrogen abstraction by excited sulphur dioxide molecules. That is, the $n \rightarrow \pi^*$ excitation of sulphur dioxide shown in Table 2 may be followed by the inter-system crossing and hydrogen abstraction by the resultant triplet from hydrocarbon giving the alkyl radical.

In order to compare the importance of these primary processes, hexyl chloride was sulphoxidized. The strength of the C—Cl bond is 64 kcal/g bond which is smaller than that of the C—H bond. The product contained sodium chloride and sodium chlorohexanesulphonate. Sodium chloride may be obtained through the energy transfer followed by the C—Cl fission, while sodium chlorohexanesulphonate may be the product via hydrogen abstraction, the molar ratio of the former to the latter being about 3:2. The ratio seems to express the ratio of homolytic C—Cl fission to hydrogen abstraction in the primary and secondary processes for hexyl chloride.

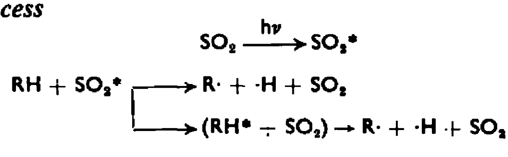


Although this ratio (3:2) cannot be applied to n-hexane, it may be reasonable to suppose at least that the primary process in n-hexane involves C—H bond cleavage by both energy transfer and hydrogen abstraction.

Furthermore, n-hexane containing sulphur trioxide yields a small amount of hexanesulphonic acid by the irradiation of UV light at room temperature. Since there is no indication of sulphur dioxide production from sulphur trioxide by the UV irradiation, the sulphonic acid should be formed by the direct reaction.

These facts may be explained by the following scheme for the primary processes:

1. *Radical chain process*



2. *Molecular process* (The first step is a well-known fact)

$$SO_2 + O_2 \xrightarrow{h\nu} SO_3$$

$$SO_3 \xrightarrow{h\nu} SO_3^*$$

$$(RH + SO_3^* \longrightarrow RSO_3H)$$

EXPERIMENTAL

Materials. *n*-Hexane (first grade) was passed through dry silica gel and then purified by Young's procedure,[13] b.p. 67·5–68°, 92 mole% purity by gas chromatography. *n*-Decane was purified by urea-adduct procedure,[14] b.p. 174°, 99 mole% purity by gas chromatography. Hexyl chloride was prepared from *n*-hexanol and thionyl chloride,[15] b.p. 133–134°, n_D^{15} 1·4178. 2,3-Dimethylbutane was prepared by Grignard synthesis starting from isopropyl bromide, b.p. 58·5°, n_D^{15} 1·3760. *p*-Chloroacetophenone was prepared by the Friedel–Crafts reaction of chlorobenzene with acetic anhydride, b.p. 126–127·5°/27 mm. Isobutyrophenone was similarly prepared from benzene and isobutyryl chloride, b.p. 106–107°/21 mm. 1-Hexene was of Phillips pure grade. Benzophenone, m.p. 48–49°, acetophenone, b.p. 195–196·5°, *p*-methylacetophenone, b.p. 117–118°/31 mm, and acetic anhydride, b.p. 140°, were purified by either recrystallization or fractionation of commercial materials of extra pure grade.

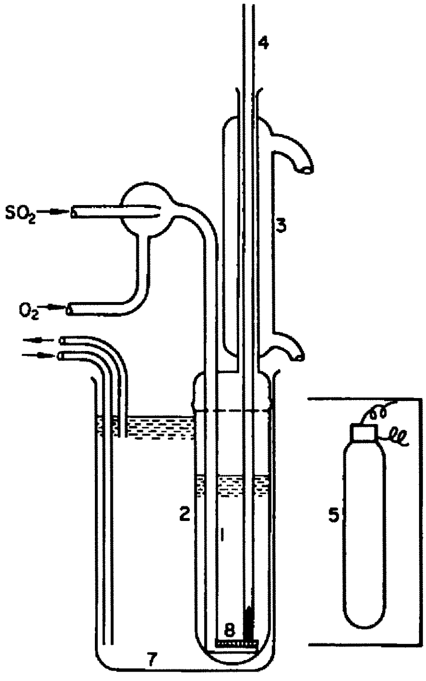


FIG. 5. Reaction apparatus for sulphoxidation.
1: Mixed gas inlet tube, 2: Reaction vessel made of Pyrex glass, 3: Cooler, 4: Thermometer, 5: Mercury lamp (Toshiba SHL-100 UV), 6: Reflector, 7: Temperature controlling bath made of Pyrex glass, 8: Sintered glass plate.

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[13] S. Young, *J. Chem. Soc.* **85**, 172 (1899).

[14] O. Frehden and G. Lazarescu, *Rev. Chim. Bucharest* **13**, 491 (1962); *Anal. Abstr.* **10**, No. 2779 (1963).

[15] F. C. Whitmore, F. A. Karnatz and A. H. Popkin, *J. Amer. Chem. Soc.* **60**, 2540 (1938).

The photochemical sulphoxidation of n*-hexane by acetic anhydride procedure. n*-Hexane (0·3 mole, 40 ml) and acetic anhydride (0·008–0·03 mole) were placed in the reaction vessel (Fig. 5); SO_2 (1–3 l./hr) and O_2 (0·5–1 l./hr) were introduced simultaneously under irradiation of UV light at 2–28° for 0·5–2 hr. Water was then added (ca. 1 ml) and the reaction mixture stirred at 40–50° for 1 hr to complete the decomposition of acetyl hexanesulphonyl peroxide. The resulting hexanesulphonic acid was extracted with water (ca. 20 ml) and the extract treated with 10% NaOH aq to pH 3. The aqueous solution was evaporated to dryness and the residue extracted with 70% EtOH aq (ca. 40 ml). The extract was evaporated to give sodium hexanesulphonate.

Sulphoxidation of n*-decane.* The sulphoxidation of *n*-decane was carried out under similar conditions, i.e. the molar ratio of *n*-decane to acetic anhydride (19:1), the rate of flow of SO_2 (1 l./hr) and O_2 (0·5 l./hr), temp (15–82°) and reaction time (1 hr).

Sulphoxidation of hexyl chloride. Sulphur dioxide (1 l./hr) and O_2 (0·5 l./hr) were introduced simultaneously into a mixture of hexyl chloride (0·15 mole, 18 g) and acetic anhydride (0·4 ml) under UV light at 27–29° for 5 hr. The resulting light brown solid material (0·5 g) contained a considerable amount of NaCl and treatment with 2% alcoholic $AgNO_3$ revealed a total chlorine content of 63·8%.

The inhibition of photochemical sulphoxidation. The photochemical sulphoxidation of *n*-hexane containing 2,3-dimethylbutane (1–10 vol%) was carried out at 14–16° for 1 hr with the molar ratio of *n*-hexane to acetic anhydride (19:1) and the rate of flow of SO_2 (1 l./hr) and O_2 (0·5 l./hr). The effect of 2,3-dimethylbutane on the yield of sodium hexanesulphonate and the inhibition with 1-hexene were similarly estimated.

The effect of aromatic ketones. Sulphur dioxide (1 l./hr) and O_2 (0·5 l./hr) were introduced simultaneously under irradiation at 16–18° for 1 hr into a mixture of acetic anhydride (0·4 ml) and *n*-hexane (20 ml) containing aromatic ketones of molar ratio 1/20–1/100. The product was sodium hexanesulphonate.

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