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Solvent Effects in the Reactions of Free Radicals and Atoms. IV. Effect of Aromatic Solvents in Sulfuryl Chloride Chlorinations[1]

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Photochemical chlorination and sulfuryl chloride chlorination give different products in the chlorination of branched-chain hydrocarbons. This has been interpreted as being due to equilibrium (1) and to the lower reactivity and greater selectivity of the SO_2Cl radical relative to the chlorine atom. In aromatic solvents little difference is noted between the products of photochlorination and sulfuryl chloride chlorination, possibly because in both types of chlorination most of the chlorine atoms are complexed with the solvent, equations 2 and 3.

It has been reported that the sulfuryl chloride chlorination of branched-chain hydrocarbons is more selective than photochlorination with molecular chlorine.[2] For example, the products of the photochlorination of 2,3-dimethylbutane at 55° indicate that a t.-hydrogen atom is 3.7 times as reactive as a p.-hydrogen atom. Sulfuryl chloride chlorination is much more selective. At 55° sulfuryl chloride reacts with 2,3-dimethylbutane in the presence of illumination to produce 1- and 2-chloro-2,3-dimethylbutane in a ratio suggesting that the t.-hydrogen atom is 10 times as reactive as a p.-hydrogen atom.[2b]

Sulfuryl chloride chlorinations are not always more selective than photochlorinations. The competitive chlorination of cyclohexane and toluene is only slightly more selective when sulfuryl chloride is used in place of molecular chlorine. At 80°, using sulfuryl chloride, a cyclohexane hydrogen atom is 3.5 times as reactive as a toluene hydrogen atom while in photochlorination the relative reactivities are 2.7 to 1.[2a] When the relative reactivities of the hydrogen atoms of toluene and *t*-butylbenzene are considered, no difference in reactivity is noticed when sulfuryl chloride or chlorine is used as the chlorinating agent. Details of these chlorinations are summarized in Table I.

TABLE I

COMPETITIVE CHLORINATION OF TOLUENE AND *t*-BUTYLBENZENE

Reactants[a]	Photochlorination, 80°	Sulfuryl chloride, 95°
t-Butylbenzene	0.659	0.672
Toluene	.707	.856
Sulfuryl chloride[b]		.121
Chlorine	.106	
Products[a]		
Benzyl chloride	0.063	0.069
Neophyl chloride[c]	.043	.044
t-Butylbenzene[d]	.616	.628
Toluene[d]	.644	.787

[a] All quantities in moles. [b] 1% by weight of benzoyl peroxide added. [c] Total alkyl chlorides minus benzyl chloride. [d] By difference.

The relative reactivities of toluene and *t*-butylbenzene were calculated from the data of Table I by the equation

$$\frac{\text{react. of } t\text{-BuC}_6\text{H}_5}{\text{react. of CH}_3\text{C}_6\text{H}_5} = \frac{\log\,[t\text{-BuC}_6\text{H}_5]_i - \log\,[t\text{-BuC}_6\text{H}_5]_f}{\log\,[\text{CH}_3\text{C}_6\text{H}_5]_i - \log\,[\text{CH}_3\text{C}_6\text{H}_5]_f} \qquad \text{(A)}$$

where the subscripts i and f represent the initial and final hydrocarbon concentrations. From equation A it is calculated that in sulfuryl chloride chlorination at 95° the relative reactivity of *t*-butylbenzene to toluene is 0.81 to 1.0, while in photochlorination at 80° the relative reactivity is 0.72 to 1. The difference between these ratios is not significant and may be due to the different temperatures employed. The sulfuryl chloride chlorination which was performed at 95° would be expected to be somewhat more selective if performed at 80°. Further evidence that photochlorination and sulfuryl chloride chlorination often yield the same products has been furnished by Walling and Miller who found that *p*-chlorotoluene was 0.69 as reactive as toluene at 70° in both photochlorination and sulfuryl chloride chlorination.[3]

The foregoing results present a puzzling picture. In some cases sulfuryl chloride is a more selective chlorination reagent than is molecular chlorine while in other cases no difference between sulfuryl chloride and molecular chlorine is noted. However, the recent findings that aromatic solvents can exert a pronounced effect upon the products of a photochlorination reaction[2b,4] also suggests an explanation to this anomaly.

Sulfuryl chloride chlorination and photochlorination using molecular chlorine have been observed to yield widely different products only in the chlorination of branched-chain hydrocarbons in the presence of aliphatic solvents. The most logical interpretation of this discrepancy is that the hydrogen-abstraction reactions are different in the two chlorination reactions. In photochlorination the hydrogen abstraction reaction is

$$Cl\cdot + RH \longrightarrow R\cdot + HCl$$

while in sulfuryl chloride chlorination hydrogen abstraction involves both chlorine atoms and the SO_2Cl radical.[2a]

$$SO_2 + Cl\cdot \rightleftharpoons SO_2Cl\cdot \qquad (1)$$

$$SO_2Cl\cdot + RH \longrightarrow SO_2 + HCl + R\cdot$$

Further evidence for the existence of the SO_2Cl radical has been provided by Kharasch and Zavist.[5]

Competitive chlorinations of aralkyl hydrocarbons in the liquid phase do not indicate an appreciable difference between photochlorination and sulfuryl chloride chlorination. Since it is now known that in the presence of aromatic hydro-

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(1) Directive Effects in Aliphatic Substitutions. XIII.

(2) (a) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031 (1955); (b) G. A. Russell, *ibid.*, **80**, 4987 (1958).

(3) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(4) G. A. Russell, *ibid.*, **79**, 2977 (1957).

(5) M. S. Kharasch and A. F. Zavist, *ibid.*, **73**, 964 (1951).

carbons chlorine atoms are mainly complexed[2b,4]

$$\mathrm{Cl}\cdot + \mathrm{Ar} \rightleftarrows \mathrm{Ar} \rightarrow \mathrm{Cl}\cdot \tag{2}$$

it is suggested that in the presence of a large excess of aromatic hydrocarbon equilibrium 1 is replaced by equilibrium 3.

$$\mathrm{SO_2Cl}\cdot + \mathrm{Ar} \rightleftarrows \mathrm{SO_2} + \mathrm{Ar}\rightarrow\mathrm{Cl}\cdot \tag{3}$$

Thus, in the presence of aromatic solvents chlorine atoms in both photochlorination and sulfuryl chloride, chlorinations are mainly complexed by the aromatic solvent and the products of either chlorination will be determined by the reactivity of the complexed chlorine atom.

As a test of this interpretation, 2,3-dimethylbutane was chlorinated with sulfuryl chloride in the presence of benzene and *t*-butylbenzene. The results, summarized in Table II, demonstrate that in the presence of aromatic solvents the products of photochlorination and sulfuryl chloride chlorination become similar. Furthermore, as the solvent effect of the aromatic hydrocarbon in photochlorination becomes larger, the difference between relative reactivities observed in photochlorination and sulfuryl chloride chlorination decreases (Table II, column 4). At 55° sulfuryl chloride is 2.7 times as selective a chlorination agent as is chlorine in the absence of any solvent except 2,3-dimethylbutane itself. In the presence of 4 *M* benzene, sulfuryl chloride is only 1.9 times as selective even though sulfur dioxide is more soluble in benzene. In the presence of 4 *M* *t*-butylbenzene, sulfuryl chloride is only 1.3 times as selective as photochlorination while in the presence of 8 *M* benzene the difference in selectivity is still less, being about 1.1 to 1.

TABLE II

PHOTOCHLORINATION AND SULFURYL CHLORIDE CHLORINATION OF 2,3-DIMETHYLBUTANE

		Relative reactivity (t./p.)		
Solvent	Temp., °C.	Photo-chlorination	Sulfuryl chloride	Sulfuryl chloride / Photo-chlorination
2,3-Dimethylbutane	55	3.7	10	2.70
Benzene, 4 *M*	55	14.5	27.8	1.91
t-Butylbenzene, 4 *M*	55	24	31.7	1.32
Benzene, 8 *M*	55	32	36	1.12
2,3-Dimethylbutane	25	4.2	12	2.85
Benzene, 8 *M*	25	49	53	1.08

Further evidence supporting this interpretation is available from studies of the deuterium-isotope effects in these reactions. Walling and Miller report the same deuterium-isotope effect when α-d_1-toluene is photochlorinated or chlorinated with sulfuryl chloride at 70° in the absence of a solvent other than the hydrocarbon itself.[3,6] This deuterium-isotope effect ($k_H/k_D = 2.1$ at 70°) is due primarily to the reactivity of the toluene–chlorine atom π-complex. The chlorination of α-d_1-toluene in an aliphatic solvent gives lower deuterium-isotope effects in both photochlorination and sulfuryl chloride chlorination.[6] A larger deuterium-isotope effect is observed in sulfuryl chloride chlorinations in carbon tetrachloride solution than for photochlorinations performed in this solvent. In the photochlorination of α-d_1-toluene at 77° the deuterium-isotope effect, k_H/k_D, is reported to be 1.30 ± 0.01, while sulfuryl chloride chlorination, involving the more selective $\mathrm{SO_2Cl}$ radical, gives a deuterium-isotope effect of 1.42 ± 0.02.[6] These results indicate: (a) different intermediate radicals in sulfuryl chloride chlorinations $\mathrm{Cl}\cdot$ and $\mathrm{SO_2Cl}\cdot$ and photochlorinations $\mathrm{Cl}\cdot$ in the presence of aliphatic solvents; (b) different intermediate radicals in photochlorinations performed in aliphatic solvents (free chlorine atoms) and aromatic solvents (solvated chlorine atoms); (c) the same radical intermediates in sulfuryl chloride chlorinations and photochlorinations (solvated chlorine atoms) performed in aromatic solvents.

TABLE III

SUMMARY OF DEUTERIUM-ISOTOPE EFFECTS IN CHLORINATION

Substrate	Solvent	Chlorinating agent	Temp., °C.	k_H/k_D
$\mathrm{(CH_3)_3C{-}H(D)}$	Isobutane	$\mathrm{Cl_2} + h\nu$	−15	1.3–1.5[a]
$\mathrm{(CH_3)_3C{-}H(D)}$	Chlorobenzene	$\mathrm{Cl_2} + h\nu$	−15	1.6–2.1[a]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Toluene	$\mathrm{Cl_2} + h\nu$	80	2.0[b]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Toluene	$\mathrm{Cl_2} + h\nu$	70	2.1[c]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Toluene	$\mathrm{SO_2Cl_2}$	70	2.1[c]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Carbon tetrachloride	$\mathrm{SO_2Cl_2}$	77	1.4[d]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Carbon tetrachloride	$\mathrm{Cl_2} + h\nu$	77	1.3[d]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Toluene	$\mathrm{Cl_2} + h\nu$	110	1.5[d]
$\mathrm{C_6H_5CH_2{-}H(D)}$	Toluene	$\mathrm{SO_2Cl_2}$	110	1.7[d]

[a] Ref. 2b. [b] Ref. 7. [c] Ref. 3. [d] Ref. 6.

Experimental

Competitive Chlorinations of Toluene and *t*-Butylbenzene.—The halogenation procedures were similar to those described previously for photochlorination[7] and sulfuryl chloride chlorination.[2a] Products of the chlorination were analyzed for total alkyl chloride by the Rauscher method[8] and for benzyl chloride in the presence of neophyl chloride by reaction with a 1:1 piperidine–ethanol solution.[7]

Sulfuryl Chloride Chlorination of 2,3-Dimethylbutane.—Apparatus described previously was employed.[2b] To 2,3-dimethylbutane (25 ml.), or a mixture of 2,3-dimethylbutane and appropriate solvent, was added 0.5 ml. of freshly distilled sulfuryl chloride. The mixture was degassed by a stream of nitrogen at the desired reaction temperature under a Dry Ice reflux condenser. After 5 minutes of degassing the sample was illuminated while still in the thermostated water-bath. Nitrogen was continuously swept through the apparatus. After about 0.5 hour sulfur dioxide no longer was evolved. Analysis of the chlorination mixture for 1- and 2-chloro-2,3-dimethylbutane by gas–liquid chromatography already has been described.[2b]

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(6) K. B. Wiberg and L. H. Slaugh, THIS JOURNAL, **80**, 3033 (1958), report a significant difference in deuterium-isotope effect observed in the photochlorination and sulfuryl chloride chlorination of α-d_1-toluene in toluene solution at 110°. At higher temperatures, interaction between chlorine atoms and the aromatic solvent should be less important, but so should interactions between sulfur dioxide and chlorine atoms.

(7) H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

(8) W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).