Free Radical Chlorination of Alkanes by Thionyl Chloride

John M. Krasniewski, Jr., and Melvyn W. Mosher*

Department of Chemistry, Marshall University, Huntington, West Virginia 25701

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The free radical chlorination reactions of thionyl chloride ($SOCl_2$) have been investigated. The reaction of thionyl chloride with alkanes proceeds when initiated with either light or benzoyl peroxide. The peroxide-initiated reactions had a chain length of about 2. Phenylazotriphenylmethane (PAT), 2,2′-azobis(2-methylpropionitrile) (AIBN), *tert*-butyl perpivilate, and di-*tert*-butyl peroxide all failed to form halogenated products. Under either photochemical or thermal conditions, the alkyl products were the chloride and the sulfonyl chloride. The selectivity for the photochemical reaction was approximately 3:1 for attack at tertiary to primary hydrogens. Relative reactivities of alkanes and substituted toluenes suggest that the hydrogen-abstracting species in both types of reaction are chlorine atoms.

The usefulness of thionyl chloride as an ionic chlorinating agent is well known.[1] However, the use of this material as a free radical chlorinating agent for alkanes has not been studied previously. As a result, it is the subject of this study.

The reaction of cyclohexane and thionyl chloride in the presence of benzoyl peroxide formed chlorocyclohexane as the major product. This reaction could be carried out without benzoyl peroxide by irradiation with tungsten lamps. In both reactions, in addition to the chlorocyclohexane, another product arising from hydrogen atom abstraction on the alkane was formed, cyclohexanesulfonyl chloride. In the thermal reaction, a chain length for the formation of the alkyl products was 1.7 ± 0.1. In the photochemical reaction, an approximate value for the quantum yield of 0.036 ± 0.009 was found for the region of 310–340 nm. In this region, the photolysis is on an end absorption of thionyl chloride.

The chlorination of 2,3-dimethylbutane by thionyl chloride in the presence of benzoyl peroxide formed a large number of products and these are reported in Table I. The major products arising from alkyl hydrogen abstraction are 2,3-dimethyl-2-chlorobutane and 2,3-dimethyl-1-butanesulfonyl chloride. The minor alkyl products are the primary chloride and the tertiary sulfonyl chloride. The tertiary sulfonyl chloride could also be a source of the tertiary chloride. Analysis of the reaction mixture showed that the concentration of 2,3-dimethyl-2-butanesulfonyl chloride decreased from a value of 0.069 *M* to 0.035 *M* at the same time that the amount of the tertiary chloride increased by 0.025 *M*. After a few days, the tertiary sulfonyl chloride could not be detected in the reaction mixture, while the amount of the primary sulfonyl chloride remained constant. The tertiary to primary selectivity of the hydrogen-abstracting species in these thermally initiated reactions was about 19:1. The three major volatile products arising from the peroxide were identified as benzene, chlorobenzene, and benzenesulfonyl chloride.

Other thermal free radical initiators were tried to see if they would also initiate these reactions. Phenylazotriphenylmethane, AIBN, di-*tert*-butyl peroxide, and *tert*-butyl perpivilate all failed to cause the formation of the alkyl chlorides or alkanesulfonyl chlorides. This selective behavior of free radical initiators has been noted elsewhere. Tanner[2] has reported that only benzoyl peroxide will cause the reaction to proceed for the free radical chlorination of alkanes by benzoyl peroxide–hydrogen chloride mixtures. Here it was postulated that the benzoyl hypochlorite, formed by addition of hydrogen chloride across the peroxide linkage, was the reactive intermediate.

A possible explanation of only benzoyl peroxide initiating the thionyl chloride reaction is that thionyl chloride is first reacting with the peroxide to form benzoyl hypochlorite and benzoyloxysulfinyl chloride. These two intermediates have been suggested previously by Pausacker for the thermal decomposition of benzoyl peroxide in the presence of thionyl chloride.[3] These two intermediates then thermally decompose to free radicals involved in the actual hydrogen-abstraction steps. This would also explain the very low value for the chain length; benzoyl peroxide is really a reactant and not just an initiator.

The decomposition of acyl hypohalites has been studied recently[4,5] and they are found to form alkyl halides when alkanes are present and/or in the absence of hydrogen-containing substrates, halobenzenes. These reactions are illustrated in Scheme I.

Scheme I

$$PhCO_2Cl \longrightarrow PhCO_2\cdot + Cl\cdot$$

$$PhCO_2\cdot \longrightarrow Ph\cdot + CO_2$$

$$Ph\cdot + PhCO_2Cl \longrightarrow PhCl + PhCO_2\cdot$$

$$Ph\cdot + RH \longrightarrow R\cdot + PhH$$

The benzoyloxysulfinyl chloride could be envisioned as a possible source for the formation of the sulfonyl chlorides, by a sequence similar to that above, and was considered by Pausacker to be the major source of benzenesulfonyl chloride.[3] If this were the case, one important reaction would be that shown in eq 1. The acyl radical

$$PhCO_2S(O)Cl + X\cdot \longrightarrow XSO_2Cl + PhCO\cdot \qquad (1)$$

would be expected to eliminate carbon monoxide and again be a source of phenyl radicals. This reaction, however, does not seem to be important, since no carbon monoxide was detected in the gaseous products by either ir or glpc.

Another possible source for the sulfonyl chlorides from the benzoyloxysulfinyl chloride could be by the sequence of Scheme II, where X is either an alkyl or aryl radical. The oxidation step could be accomplished by either the acyl hypochlorite or benzoyl peroxide. In the first case, the acid chloride would be formed, while, in the second, benzoic anhydride would result. The oxidation process would seem likely, since sulfinyl chlorides are known to be oxidized to the sulfonyl chlorides by hypohalite ions.[6]

Scheme II

$$X\cdot + PhCO_2S(O)Cl \longrightarrow XSOCl + PhCO_2\cdot$$

$$XSOCl + \text{oxidizing agent} \longrightarrow XSO_2Cl$$

A third pathway for the formation of the products would be similar to that reported for the Reed reaction.[7] Scheme III, where X is either an alkyl or aryl radical. These reactions could arise by a series of steps involving hydrogen abstraction by chlorine atoms initially formed from the acyl hypochlorite. In this case, hydrogen chloride

Table I
Reaction Mixture Composition for Representative Reactions of Thionyl Chloride with 2,3-Dimethylbutane[a]

Compd	Reactions with benzoyl peroxide				Photochemical reactions	
	1	2	3	4[b]	1	2
Benzene	0.034	0.045	0.020	0.004		
2-Chloro-2,3-dimethylbutane	0.185	0.195	0.348	0.00004	0.238	0.239
1-Chloro-2,3-dimethylbutane	0.014	0.023	0.026	0.00001	0.045	0.032
Chlorobenzene	0.050	0.023	0.056	0.002		
2,3-Dimethylbutane-1-sulfonyl chloride	0.025	0.038	0.083	0.110	0.405	0.360
2,3-Dimethylbutane-2-sulfonyl chloride	0.006	0.003	0.006	0.004	0.005	0.017
Benzenesulfonyl chloride	0.042	0.119	0.136	0.164		
Chlorinated benzoic acids[c]	0.073	0.087	0.036	0.002		
Benzoyl chloride–benzoic anhydride	0.410	0.508	0.715	0.293		
Thionyl chloride[d]	1.680	0.831	1.342	1.25	1.190	0.738
Benzoyl peroxide[d]	0.341	0.369	0.502	0.268		
Material balance phenyl	88	105	96	87		

[a] All concentrations are in moles per liter in 2,3-dimethylbutane. Experimental errors on all molarities are less than 6%. [b] SO_2 added to 1.77 *M*. [c] The ratio of the ortho:meta:para isomers was 1:1:1. [d] Starting concentrations.

Table II
Relative Reactivities of Several Substrates of Different Structures and Substituents toward Thionyl Chloride under Thermal and Photochemical Conditions, Compared with the Values Obtained for Chlorine

Substrate	Registry no.	Thionyl chloride[a]	Thionyl chloride[b]	Chlorine
		Cyclohexane as Standard		
Cyclohexane	110-82-7	1.00	1.00	1.00
Cyclopentane	287-92-3	2.32 ± 0.06	1.35 ± 0.13	0.82 ± 0.06
2,3-Dimethylbutane	79-29-8	6.88 ± 0.10	1.05 ± 0.11	0.75 ± 0.11
2,2,3,3-Tetramethylbutane	594-82-1	0.38 ± 0.05	0.42 ± 0.09	0.33 ± 0.10
Toluene	108-88-3	0.31 ± 0.05	0.41 ± 0.06	0.27 ± 0.08
1-Chlorobutane	109-69-3	0.36 ± 0.11	0.29 ± 0.09	0.25 ± 0.10
Perdeuteriocyclohexane	1735-17-7		0.85 ± 0.08	0.78 ± 0.08
		Toluene as Standard		
Toluene		1.00	1.00	1.00
p-Xylene[c]	106-42-3	1.60 ± 0.09	1.65 ± 0.19	1.60 ± 0.23
m-Xylene[c]	108-38-3	1.11 ± 0.9	1.13 ± 0.10	1.22 ± 0.22
p-Chlorotoluene	106-43-4	0.65 ± 0.09	0.46 ± 0.11	
m-Chlorotoluene	108-41-8		0.68 ± 0.15	0.59 ± 0.09

[a] Benzoyl peroxide present. [b] Photochemically. [c] Statistically corrected.

Scheme III

$$X\cdot + SO_2 \longrightarrow XSO_2\cdot$$

$$XSO_2\cdot + Cl_2 \longrightarrow XSO_2Cl + Cl\cdot$$

would be a major product and react with benzoyl peroxide to product the acyl hypochlorite and benzoic acid.[2] The benzoic acid formed would be converted into the acid chloride by the excess thionyl chloride present (eq 2). The

$$PhCO_2H + SOCl_2 \longrightarrow PhCOCl + SO_2 + HCl \qquad (2)$$

chlorine molecules would arise by the reaction of a positive halogen compound with hydrogen chloride. This type of process has been well studied in the case of *N*-chlorosuccinimide[8] and reported for *N*-chloro amines.[9,10]

An alternate or possible competing route for the formation of chlorine and sulfur dioxide could be the chain transfer of the radical, X, with thionyl chloride. The resulting previously unreported chlorosulfinyl radical, SOCl·, might be expected to be in equilibrium with sulfur monoxide and chlorine atoms, similar to that reported by Russell for the equilibrium of $SO_2Cl\cdot$ radicals.[11] If this equilibrium is involved, the sulfur monoxide is known to disproportionate into elemental sulfur and sulfur dioxide.[12,13] The sulfuryl chloride which has been detected as a reaction product could arise by the equilibrium involving sulfur dioxide and molecular chlorine.[11]

Of the three routes outlined for the formation of the products, we believe that the third pathway is operative. The amount of benzene, a product derived from hydrogen abstraction of phenyl radicals, is very low, approximately one-sixth the amount of alkyl products arising from hydrogen atom abstraction. The other hydrogen abstraction most likely is by chlorine atoms which favor the formation of hydrogen chloride, and as a result sulfur dioxide, by eq 2. As the sulfur dioxide concentration increases, the reactions in Scheme III should become more important. This scheme was confirmed by the fact that, in a set of reactions with sulfur dioxide added, the amount of the alkanesulfonyl chloride was greatly enhanced at the expense of the alkyl chloride (Table I, entry 4).[14] In these reactions, the radical formed by hydrogen abstraction would have a greater probability of attack on the sulfur dioxide than to chain transfer with the hypochlorite.

The values of the relative rates of reaction for a number of toluenes and alkanes were determined and are presented in Table II. The use of relative reactivities as a probe for the study of intermolecular selectivities of a specific radical has the advantage that the ratio of rate constants is obtained from the determination of the relative concentrations of the substrates and that this value is not affected by the subsequent fate of the intermediates or products involved. The values obtained for relative rates of reactions are similar to those for chlorine under photochemical conditions. The exceptions are 2,3-dimethylbutane and cyclopentane. A possible explanation comes from the literature. It has been found previously in systems of benzoyl peroxide–hydrogen chloride that large amounts of reversible hydrogen abstraction from hydrogen chloride by alkyl radicals are present.[2] Reversible hydrogen abstraction has been shown to cause increased reactivities of certain compounds in relative rate determinations.[2,15] With iodobenzene dichloride, an increase in the reactivity of 2,3-dimethylbutane relative to cyclohexane has been noted.[15] Substrates containing halogens and/or aromatic rings, are not affected.[16]

The photochemical reaction was also studied to gain an insight as to the hydrogen-abstracting radical under these conditions. In the reaction of 2,3-dimethylbutane with thionyl chloride, only four products were detected, and these are reported in Table I. The tertiary to primary selectivity for the abstracting radical in the photochemical reaction was found to be 3.2:1.0 for the reaction run at 42°. This value for the selectivity is similar to that reported for molecular chlorine.[11,17]

To gain a better probe as to the nature of the abstracting species, the relative reactivities for the chlorination using thionyl chloride were obtained and reported in Table II.

The values in the table for thionyl chloride are similar to those reported for chlorine except for cyclopentane. A value for the primary:secondary:tertiary selectivity calculated from the relative reactivities is 1:3.6:16 for thionyl chloride compared to a selectivity of 1:4.6:14 for molecular chlorine. These values are similar to other values for the selectivity calculated from relative rates of reaction data for chlorine atoms.[17] The relative reactivities for the cyclohexane and perdeuteriocyclohexane allowed for the calculation of a deuterium isotope effect. This value is 1.25, which is within experimental error of the value obtained for molecular chlorine in this study and reported in the literature.[15,18]

The relative rates of reaction of thionyl chloride with the substituted toluenes allowed for a Hammett plot to be made. A ρ value of -0.70 was obtained for the reactions involving thionyl chloride, while a value of -0.76 was obtained for molecular chlorine. Both of the values compare very well with previous literature values for chlorine atoms as the hydrogen-abstracting species.[19,20]

The following mechanism (Scheme IV) is suggested from these hydrogen atom abstractions by the reactive intermediate from thionyl chloride. In the reaction of thionyl chloride with acids to form the acid chloride, α-chlorination has been noted. The chlorination has been suggested as arising from a mechanism involving chlorine molecules formed from the photolysis of thionyl chloride,[21] similar to that reported here in steps 1, 4, and 8.

Scheme IV

$$\mathrm{SOCl_2 \longrightarrow Cl\cdot + SOCl\cdot} \tag{1}$$

$$\mathrm{RH + Cl\cdot \longrightarrow R\cdot + HCl} \tag{2}$$

$$\mathrm{RH + SOCl\cdot \longrightarrow R\cdot + HCl + [SO]} \tag{3}$$

$$\mathrm{2SOCl\cdot \longrightarrow SO_2Cl_2 + S} \tag{4}$$

$$\mathrm{SO_2Cl_2 \longrightarrow Cl\cdot + SO_2Cl\cdot} \tag{5}$$

$$\mathrm{SO_2Cl\cdot \longrightarrow Cl\cdot + SO_2} \tag{6}$$

$$\mathrm{RH + SO_2Cl\cdot \longrightarrow R\cdot + HCl + SO_2} \tag{7}$$

$$\mathrm{SO_2Cl_2 \longrightarrow SO_2 + Cl_2} \tag{8}$$

The calculated ρ value for thionyl chloride and the relative reactivities indicate that the major hydrogen-abstracting species is chlorine atoms. These could arise in the homolysis of the S–Cl bond of thionyl chloride. The abnormally high value for the relative reactivity of cyclopentane compared to that of the other compounds studied could be explained by abstraction by the $\mathrm{SO_2Cl\cdot}$ radical (eq 3–5). This is supported by the relative reactivity of cyclopentane to cyclohexane found in the literature[22] for sulfuryl chloride as the chlorinating agent.

The well-known equilibrium of chlorine atoms with sulfur dioxide would favor hydrogen atom abstraction by chlorine atoms when deactivated substrates are employed. Cyclopentane has been shown by Bunce[23] to react more rapidly than statistics would suggest relative to cyclohexane with hydrogen-abstracting radicals that are more selective than chlorine. Such is the case with this substrate in the thionyl chloride reactions. With more reactive substrates, a larger amount of hydrogen abstraction would be by the $\mathrm{SO_2Cl\cdot}$ radical, indicating that eq 7 is important only with this type of substrate. The slightly higher reactivity of 2,3-dimethylbutane than that of cyclohexane for thionyl chloride can also be explained along these lines.

In conclusion, it appears that the thermal reaction of thionyl chloride, benzoyl peroxide, and hydrocarbons proceeds by a nonchain process with chlorine atoms as the hydrogen-abstracting species. In the photochemical reactions, thionyl chloride again forms chlorine atoms, which are responsible for hydrogen atom abstraction.

Experimental Section

All compounds were commercially available unless otherwise indicated. Thionyl chloride was purified by either the method of Trager[24] or that of Friedman and Witter.[25] The primary sulfonyl chloride, 2,3-dimethylbutane-1-sulfonyl chloride, was prepared from the hydrocarbon and sulfonyl chloride with an excess of added sulfur dioxide, amide mp 47–48° (lit.[26] mp 48–49°). Cyclohexanesulfonyl chloride was prepared similarily, amide mp 90–91° (lit.[27] mp 93–94°).

General Procedure. Reactions were carried out in sealed Pyrex ampoules which had been doubly degassed by the freeze–thaw method. The ampoules were allowed to stand in a constant-temperature bath (98 ± 3°) for an appropriate period and were opened after being cooled to 77°K. A weighed amount of an appropriate standard was added to the opened tubes.

Photoinitiated reactions were also carried out in Pyrex ampoules as described above. These ampoules were placed in a water bath at 41 ± 0.5°; and photolyzed with two 150-W tungsten lamps. At appropriate times, the tubes were removed and treated as above.

All values obtained are the results of at least duplicate, and in many instances triplicate, experimental runs and subsequent analysis. Analysis was mainly be means of glpc on a Hewlett-Packard F & M Model 700 gc using either column A (6 ft × 0.25 in. 20% silicon gum rubber SE-30 on 60/80 Chromosorb W), column B (6 ft × 0.25 in. 20% DEGS on 60/80 acid-washed Chromosorb G), column C (6 ft × 0.25 in. 10% silicon gum rubber SE-52 on 60/80 Chromosorb G), or column D (6 ft × 0.25 in. 10% di-*n*-nonyl phthalate on 60/80 Chromosorb G). Products were identified by comparison of their glpc retention times with those of authentic samples. Samples were collected by preparative glpc and identified by comparison of their nmr, ir, and/or mass spectra with those of authentic samples, except for 2,3-dimethyl-2-butanesulfonyl chloride, which could not be isolated.

Yields reported are based either on the amount of benzoyl peroxide employed in the thermal reactions, or upon reacted thionyl chloride in the case of the photochemical reactions, unless otherwise stated.

Reaction of Thionyl Chloride with Cyclohexane. I. Solutions of equimolar amounts of thionyl chloride and benzoyl peroxide (0.33 *M*) in cyclohexane were heated at 98 ± 3° for 72 hr. After this time, 2,3-dibromobutane was added as an additional standard and the mixture was analyzed on column A or B isothermally at 80°, until the standard had come off the column. At this time, the temperature was turned to 160°. The only alkyl products obtained were chlorocyclohexane (60.5 ± 0.4%, chain length 1.00 ± 0.1) and cyclohexanesulfonyl chloride (17.9 ± 0.3%, chain length 0.65 ± 0.08). Three other volatile products were detected as arising from benzoyl peroxide, chlorobenzene (7.7 ± 0.1%), benzene (3.5 ± 0.1%), and benzenesulfonyl chloride (16.5 ± 0.3%).

II. In the photochemical reactions, a degassed solution of thionyl chloride (1.14 M) in cyclohexane was irradiated for 17.5 hr. Analysis was by glpc on either column A or column B isothermally at 80°, until the standard had come off the column, and then the temperature was increased to 160°. The only two products detected were cyclohexane (47.2 ± 1.0%) and cyclohexanesulfonyl chloride (40.0 ± 0.8%). These yields were based upon thionyl chloride reacted.

III. In separate triplicate reactions, degassed solutions of equimolar amounts of each of the following thermal free radical initiators and thionyl chloride in a 15 molar excess of cyclohexane were heated at 90° for 36 hr. The tubes were opened and the reaction mixtures were analyzed on column A and in II above. No detectable amounts of cyclohexanesulfonyl chloride or the chlorocyclohexane were found. The initiators used were tritylazobenzene, di-*tert*-butyl peroxide, 2,2′-azobis(2-methylpropionitrile), and *tert*-butyl perpivalate.

IV. Quantum Yield. Sealed, degassed ampoules of thionyl chloride (1.58 M) in cyclohexane were irradiated by two 150-W tungsten lamps in a bath maintained at 41.5 ± 1.0°. At the same time, a set of sealed degassed ampoules containing 2 ml of a benzophenone (0.35 M) in 2-propanol solution were also irradiated in the same bath with the same light source. The benzophenone–2-propanol tubes and the thionyl chloride tubes were removed at various times and cooled to 77°K. In the case of the chlorination tubes, analysis for alkyl products was made by glpc on column A as before. In order to analyze the actinometer reaction tubes, a modified method of Pitts[28] was employed. The quantum yield obtained was 0.0036 ± 0.009.

Reaction of Thionyl Chloride with 2,3-Dimethylbutane. I. Degassed solutions of approximately equimolar amounts of thionyl chloride and benzoyl peroxide in excess 2,3-dimethylbutane were heated at approximately 100° for 72 hr. Analysis by glpc on column A with 2,2-dibromobutane as the added standard indicated the presence of seven products. Four other compounds were found in the reaction mixture that could not be detected by glpc. These were benzoic acid and the 3-monochlorinated benzoic acids. These were identified and isolated by evaporation of the reaction mixture nearly to dryness. This was taken up in ether and washed successively with water, 10% sodium hydroxide, and 10% hydrochloric acid. The aqueous layers from the last two extractions were neutralized and extracted with ether. The ether was removed after drying over sodium sulfate. The water layer was evaporated to dryness. The only materials found in the three fractions were benzenesulfonyl chloride and the benzoic acids. The acids were identified by treatment with (1) diazomethane and glpc analysis on column D or (2) thionyl chloride followed by methanol and glpc analysis on column C.

To determine if the benzoic acids arose from either the acid chloride and/or the anhydride, a reaction tube was opened and the mixture was poured into methanol. Methyl benzoate was detected after the solution was heated under reflux for approximately 30 min, and then analyzed upon column C. Infrared spectral analysis indicated that the ratio of the anhydride to the acid chloride was 0.7.

The molar amounts of these products are listed for three representative reactions in Table I.

II. Degassed solution of thionyl chloride (about 1 M) in 2,3-dimethylbutane was irradiated for 1 week at 40°. Analysis by glpc on column A, using 1,2-dibromobutane as an added standard, indicated the presence of four products. The molar amounts of these compounds are also listed in Table I. These experiments were repeated using trichloroethylene as a chlorine trap after the method of Walling.[29] The results between these two experiments were within experimental error, although the yield was considerable less.

III. Gaseous Products. The reaction of thionyl chloride and benzoyl peroxide in 2,3-dimethylbutane was run in a degassed ampoule equipped with a break seal. After the reaction was complete, the reaction mixture was opened into a vacuum line and allowed to warm to room temperature. A gas-phase infrared spectrum was obtained on the gases, in a 10-cm gas infrared cell. By their characteristic absorptions, the following compounds were identified, although not quantitated: carbon dioxide,[30], sulfur dioxide,[30] and sulfuryl chloride.[31] The gaseous products were also analyzed on a Porapak Q glpc column. No detectable amount of carbon monoxide was present.

Competitive Reactions. Relative reactivities were determined by the methods previously reported from this laboratory[17,22] for the photochemical and thermal reactions. These values are reported in Table II. These experiments were repeated with trichloroethylene as a chlorine-atom trap, and the results were within experimental error of those obtained in the other reactions.

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Registry No.—Thionyl chloride, 7719-09-7.

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