The Free Radical Mechanism of the Decomposition of Alkylsulfonyl Chlorides in Liquid Cyclohexane

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Abstract: The kinetics and mechanism of the γ radiation induced free radical chain decomposition of alkylsulfonyl chlorides ($R'SO_2Cl$) dissolved in cyclohexane were studied at 120°. It was found that significant decomposition of $R'SO_2$ radicals did not occur and that the rates of consumption of $R'SO_2Cl$ and the rate of formation of chlorocyclohexane were equal. The latter was thus used to monitor the rate of formation of sulfinic acids. The following rate constants for hydrogen abstraction by $R'SO_2$ radicals from cyclohexane were estimated at 120°: 303 ± 8, 245 ± 8, and 145 ± 7 l./(mol sec) for R = Me, *n*-Pr, and *n*-Bu, respectively. Competition between $R'SO_2Cl$ and C_2Cl_4 for the cyclohexyl radicals was utilized for the determination of the rate constants of chlorine abstraction from $R'SO_2Cl$ by cyclohexyl radicals which were found to be: $2.27 \pm 0.09 \times 10^6$, $1.48 \pm 0.11 \times 10^6$, and $1.43 \pm 0.03 \times 10^6$ l./(mol sec) for R′ = Me, *n*-Pr, and *n*-Bu, respectively. The results of this work seem to indicate that the reaction between alkylsulfonyl radicals and hydrocarbons could significantly contribute to the observed rates of sulfinic acid formation in gas phase photolytic studies of paraffin hydrocarbon–SO_2 systems.

The kinetics and mechanism of reactions between paraffin hydrocarbons (RH) and SO_2 have been studied mainly in the gas phase by photochemical initiation.[1-4] As was originally suggested by Dainton and Ivin[1] sulfinic acids appear to be among the main products of photolysis. However, particularly in systems where the RH/SO_2 concentration ratio is small, other products, especially those containing more than one SO_2 unit, are also formed. The mechanism of the photochemical reactions in the $RH-SO_2$ system is not fully understood, mainly because of experimental difficulties in conducting accurate kinetic studies. These difficulties are caused by the instability of the products and aerosol formation almost at the onset of the photochemical reaction.

As yet, agreement has not been reached as to the exact nature of the excited SO_2 species that is involved in the chemical reaction.[5-6] It seems that the sequence of reactions initiated by hydrogen abstraction from RH by some excited species SO_2^* is to be favored over the direct insertion mechanism.[4]

$$SO_2^* + RH \longrightarrow HSO_2 + R$$
$$\longrightarrow RSO_2H$$

The R radicals thus formed can either combine with the SO_2H radicals or add to SO_2 to give alkylsulfonyl radicals which subsequently abstract hydrogen from RH.

$$R + SO_2H \longrightarrow RSO_2H$$
$$R + SO_2 \longrightarrow RSO_2$$
$$RSO_2 + RH \longrightarrow RSO_2H + R$$

Both routes lead to the formation of sulfinic acids.

Good and Thynne[7] determined the Arrhenius parameters for the addition of methyl and ethyl radicals to SO_2. Subsequent studies of Calvert, Slater, and Gall[8] have shown that the system investigated by Good and Thynne was more complex than originally suggested. Only recently the rate of addition of methyl radicals to SO_2 was directly determined by James *et al.*[9] All the data obtained in the kinetic studies indicate that the addition of alkyl radicals to SO_2 is fast and that it could be one of the routes of SO_2 removal from the polluted atmosphere.[10] So far quantitative kinetic studies of the reactions of RSO_2 radicals have not been made.

The present work was initiated in an attempt to obtain rate data for the reactions of alkylsulfonyl radicals with paraffin hydrocarbons. These data could help clarify the results of previous investigators and give information as to the potential importance of the reactions of RSO_2 radicals in the polluted atmosphere. Liquid phase radiolysis was shown by us to be a convenient method for the study of free radical chain reactions.[11] This method is free from some of the previously mentioned complications encountered in the gas phase studies. Also, liquid phase kinetic data for transfer reactions can be easily extrapolated to the gas phase.[12] Alkylsulfonyl chlorides were chosen as a source of RSO_2 radicals in a method similar to that employed by Davies, *et al.*, in their esr studies.[13]

Experimental Section

Materials: Cyclohexane (Phillips, research grade), C_2Cl_4 (Matheson, spectrograde), and $MeSO_2Cl$ (Fluka, puriss.) were used as received. *n*-$PrSO_2Cl$ and *n*-$BuSO_2Cl$ (Eastman) were distilled under vacuum and the middle cut was used.

Procedure and Analysis. Liquid samples were degassed and then placed in a temperature-controlled silicon-oil bath held at 120 ± 0.3° and irradiated at a dose rate of 1.56×10^{15} eV/(ml sec). Gas chromatography was employed for product separation and analysis. Intially, Ucon and Silicon Gum Rubber SE-30 columns were used in unsuccessful attempts to separate the sulfinic acids. Since the sulfinic acids that were isolated up to now show thermal instability[14,15] it is quite possible that our failure was caused by the decomposition of the sulfinic acids on the gas-chromatographic column. Subsequent product analysis was carried out on a 6 ft by ⅛ in. stainless steel column, packed with Silicon Oil DC-200 on Chromosorb W, and temperature programmed from 80 to 150°. A gas chromatograph (Hewlett-Packard 5750), equipped with a flame ionization detector, was used.

In order to determine the thermal stability the samples were held for 2 hr at 120°. Thermal decomposition was found to be negligible when compared to the rates of product formation in the radiolytic system.

Results

The results of the radiolysis of alkylsulfonyl chloride ($R'SO_2Cl$) solutions in cyclohexane are given in Table I. In these experiments conversion did not exceed 5% and therefore material balance could not be determined accurately. In additional experiments (not given in Table I) that were done at 30–40% conversion, the rate of formation of chlorocyclohexane was found to be equal within ±10% to the rate of consumption of $R'SO_2Cl$. This result verified our initial observation that R′Cl products were not formed in appreciable yields under our experimental conditions. In the "high conversion experiments" the rate of formation of chlorocyclohexane was considerably slowed down. However, products other than those formed at low conversion

Table I. Formation of Chlorocyclohexane in Solutions of Sulfonyl Chlorides in Cyclohexane Irradiated at 120°[a]

[R′SO$_2$Cl], mol/l.	Irr time, min	G, mol/100 eV	d[RCl]/dt × 10^6, mol/(l. sec)	No. of runs
		R′ = Me		
0.087	5	350	9.05	2
0.128	10	318	8.22	2
0.256	5	343	8.85	2
0.256	10	323	8.36	2
0.256	15	320	8.28	4
		R′ = n-Pr		
0.113	10	267	6.89	2
0.165	10	276	7.13	2
0.225	5	270	6.98	2
0.225	10	253	6.54	2
0.225	15	260	6.71	2
		R′ = n-Bu		
0.085	10	156	4.04	1
0.100	10	168	4.35	2
0.142	5	147	3.81	2
0.142	10	150	3.90	2
0.142	15	162	4.19	3

[a] G(bicyclohexyl) = 0.3 ± 0.05 in all experiments.

were not observed. In all the experiments the yield of bicyclohexyl was very low, G(bicyclohexyl) = 0.3 ± 0.05.

In order to determine the rate of chlorine abstraction from alkylsulfonyl chlorides, solutions of C_2Cl_4 and $R'SO_2Cl$ in cyclohexane were irradiated. The only detectable liquid products formed in these systems were chlorocyclohexane and trichlorovinylcyclohexane, RC_2Cl_3. A good material balance was observed in these experiments which are summarized in Table II.

Discussion

Kinetic Scheme. The G values of chlorocyclohexane formation observed by us in the RH-$R'SO_2Cl$ systems are considerably higher than the radiolytic yield of radicals in cyclohexane, G(radicals) = 5.7.[16] Hence, RCl and sulfinic acids have to be formed by a free radical chain mechanism described by the following reaction scheme.

Initiation (schematic)

$$2RH \longrightarrow 2R + \text{products} \tag{1}$$

Propagation

$$R + R'SO_2Cl \longrightarrow RCl + R'SO_2 \tag{2}$$

$$R'SO_2 + RH \longrightarrow R'SO_2H + R \tag{3}$$

Termination

$$2R'SO_2 \longrightarrow (R'SO_2)_2 \tag{4}$$

$$R'SO_2 + R \longrightarrow R'SO_2R \tag{5}$$

$$R + R \longrightarrow R_2 \tag{6}$$

$$\longrightarrow RH + \text{cyclohexane} \tag{7}$$

Additional reactions that could take place in the $R'SO_2Cl$-RH system are

$$R'SO_2H \longrightarrow RH + SO_2 \tag{8}$$

$$R'SO_2 \longrightarrow R' + SO_2 \tag{9}$$

$$R' + R'SO_2Cl \longrightarrow RCl + R'SO_2 \tag{10}$$

$$R' + RH \longrightarrow R'H + R \tag{11}$$

$$R' + SO_2 \longrightarrow R'SO_2 \tag{12}$$

$$R + SO_2 \longrightarrow RSO_2 \tag{13}$$

$$RSO_2 + R'SO_2Cl \longrightarrow RSO_2Cl + R'SO_2 \tag{14}$$

$$RSO_2 + RH \longrightarrow RSO_2H + R \tag{15}$$

However, the occurrence of these reactions can be excluded on the following grounds. In the liquid phase studies of the RH-SO_2 systems it has been qualitatively shown that the addition of alkyl radicals to SO_2 is a fast reaction.[17,18] Therefore, in the present system we would expect RSO_2Cl to be formed as a result of reactions 8, 9, 13, and 14. Also, if reaction 9 takes place then R′Cl products would be formed by reaction 10 and R′H by reaction 11. The formation of these products in appreciable yields was not observed by us. The conclusion that reactions 8-15 are of marginal importance in the above systems is supported by the material balance determination.

The Determination of the Rate Constant of Chlorine Abstraction from Alkylsulfonyl Chlorides. Reaction 2. Competitive experiments in $R'SO_2Cl$-C_2Cl_4 solutions in cyclohexane were carried out in order to determine the rate constant for the formation of the $R'SO_2$ radicals. In the RH-C_2Cl_4 system, RC_2Cl_3 is formed by a chain mechanism, whose propagation step is described by reactions 16-18. The rate

$$R + C_2Cl_4 \longrightarrow RC_2Cl_4 \tag{16}$$

$$RC_2Cl_4 \longrightarrow RC_2Cl_3 + Cl \tag{17}$$

$$Cl + RH \longrightarrow HCl + R \tag{18}$$

constant ratio is given by expression I provided that RCl and RC_2Cl_3 are the only products formed by the reaction between the cyclohexyl radicals and the two solutes, as was

$$k_2/k_{16} = \log\left[1 - \frac{[RCl]}{[RSO_2Cl]_0}\right] \Big/ \log\left[1 - \frac{[RC_2Cl_3]}{[C_2Cl_4]_0}\right] \tag{I}$$

found by us. The rate constant ratios estimated from the data of Table II and expression I are given in Table III. The k_2 values given in that table were obtained by substituting the value of 4.18 × 10^4 l./(mol sec) for k_{16}. The latter value was calculated from the previously determined Arrhenius parameters of reaction 16.[11] It seems that the present data are not sufficient to establish whether the stability of the $R'SO_2$ radicals causes the observed difference in reactivity.

The results of the competitive experiments can be used for the estimation of the steady state concentrations of cyclohexyl radicals, $[R]_s$, at given $R'SO_2Cl$ and C_2Cl_4 concentrations. Values for $[R]_s$ calculated from expression II are given in Table II.

$$[R]_s = [RC_2Cl_3]/k_{16}[C_2Cl_4]t \tag{II}$$

It is instructive to compare these values with the maxium steady state concentration, $[R]_{max}$, of cyclohexyl radicals in the radiolysis of pure cyclohexane. $[R]_{max}$ is given by expression III where $G[R]$, the yield of radicals in cyclohex-

$$[R]_{max} = \{\alpha G[R]/2[k_6 + k_7]\}^{1/2} \tag{III}$$

ane, is taken as 5.7[16] and α is a factor that converts G values into rates of formation in units of molecules per liter second. At the applied dose rate α is 2.6 × 10^{-8}. The assumption that the reaction between cyclohexyl radicals is diffusion controlled leads to a $k_6 + k_7$ value of 6.89 × 10^9 l./(mol sec) at 120°. This value was obtained by taking $k_6 + k_7$ equal to 1 × 10^9 l./(mol sec) at 25° [19] and the activation energy of diffusion in cyclohexane as equal to 4.54 kcal.[20] Upon substitution of the above estimated values into expression III $[R]_{max}$ is found to be 3.9 × 10^{-9} mol/l. Comparison of $[R]_{max}$ with the steady state concentrations of cyclohexyl radicals, given in Table II, indicates that in the presence of $R'SO_2Cl$ and C_2Cl_4 the concentration of cyclohexyl radicals is drastically reduced.

From previous studies[11] of the RH-C_2Cl_4 system we know that at 120° and at the tetrachlorethylene concentration used in the present work $[R] \gg [RC_2Cl_4]$. Hence,

Table II. The Formation of Chlorocyclohexane (RCl) and Trichlorovinylcyclohexane (RC_2Cl_3) in Solutions of Tetrachloroethylene and Alkylsulfonyl Chlorides in Cyclohexane Irradiated at 120°[a]

R′	Irr time, min	$[R'SO_2Cl]_0$, mol/l. × 10^3	$[C_2Cl_4]_0$, mol/l. × 10^3	$[RCl]_f$, mol/l. × 10^3	$[RC_2Cl_3]_f$, mol/l. × 10^4	$-d[RCl]/d[R'SO_2Cl]$	$[R]_s$,[b] mol/l. × 10^{11}
Me	69	64.3	250	16.7	13.4	0.96	3.10
	84	64.3	250	18.3	16.1	1.02	3.06
	47	128.6	250	14.5	5.56		1.89
	81	128.6	250	21.4	8.14	0.98	1.60
n-Pr	32	123	200	12.4	5.63	1.09	3.20
	30	225	200	11.3	2.84	1.12	1.72
	63	225	200	22.3	6.36	0.98	1.83
n-Bu	60	35.6	500	10.8	52.7	0.99	7.00
	60	35.6	500	11.1	55.1	0.98	7.32
	60	71.2	500	15.7	35.5	1.03	3.10

[a] $[R'SO_2Cl]_0$ and $[C_2Cl_4]_0$ denote initial concentrations while $[RC_2Cl_3]_f$ and $[RCl]_f$ stand for final concentrations. [b] Calculated from eq II.

Table III. Rate Constants of the Reactions Involved in the Propagation Step of the Formation of Sulfinic Acids in Cyclohexane at 120°

R′	k_2/k_{16}	k_2,[a] l./(mol sec) × 10^{-6}	$(k_3/2k_4)^{1/2}$, (l./mol sec)$^{1/2}$ × 10^3	k_3,[b] l./(mol sec)
Me	54.3 ± 2.1	2.27 ± 0.09	2.59 ± 0.07	303 ± 8
n-Pr	35.4 ± 2.6	1.48 ± 0.11	2.09 ± 0.07	245 ± 8
n-Bu	34.3 ± 0.7	1.43 ± 0.03	1.24 ± 0.06	145 ± 7

[a] k_{16} at 120° taken as 4.18 × 10^4 l./(mol sec) calculated from data of ref 11. [b] $2k_4$ assumed to be equal to that of cyclohexyl radicals and estimated as in ref 11.

under the experimental conditions of the competitive experiments, the $R'SO_2$ radicals comprise about 99% of the radicals. The importance of this conclusion lies in the fact that it is applicalble also to the binary $R'SO_2Cl$-RH systems.

The Determination of the Rate Constant of Sulfinic Acid Formation. Reaction 3. Based on the proposed reaction mechanism and the observed material balance the rate of formation of chlorocylohexane, R_{RCl}, and the rate of formation of the sulfinic acids, $R_{R'SO_2H}$, in the RH-$R'SO_2Cl$ systems have to be equal. Thus, in terms of the proposed reaction scheme, the rate of formation of the sulfinic acids should be given by expression IV. In the derivation of this

$$R_{RCl} = R_{R'SO_2H} = \left[\frac{\alpha G[R]k_3}{2k_4}\right]^{1/2}[RH] \qquad (IV)$$

equation it has been assumed that practically all the radicals in the system are those of $R'SO_2$ as was shown in the previous section. Further experimental evidence supporting this assumption is provided by the low yields of bicyclohexyl found by us, $G[R_2] = 0.3 \pm 0.05$. This yield should be compared with $G[R_2]$ of 0.3, for bicyclohexyl that is formed in processes that are not affected by the presence of solutes,[21] and with $G[R_2]$ of 1.9, in pure cyclohexane that is independent of temperature.[22] Inspection of the results of Table I shows that the rate of formation of chlorocyclohexane is independent of the concentration of the alkylsulfonyl chloride, as required by expression IV.

In Table III are given the $k_2/[2k_4]^{1/2}$ values that were calculated with the use of expression IV. In order to calculate from these ratios the value of k_2 it is necessary to know the value of k_4. Unfortunately, the rate constants for the combination of alkylsulfonyl radicals have not been determined. In the derivation of the k_2 values of Table III it has been assumed that k_4 and $k_6 + k_7$ are equal. It is quite possible that the reaction between $R'SO_2$ radicals is considerably slower than the reaction between alkyl radicals. However, even if k_4 were over-estimated by two orders of magnitude, which we feel would be the maximum difference in the combination rate constants, the values of k_3 estimated by us would be accurate within an order of magnitude. In any case, the chain mechanism of RCl formation coupled with the requirement that the concentration of alkylsulfonyl radicals is much higher than that of the cyclohexyl radicals, necessarily leads to the conclusion that k_3 is lower than k_2 by several orders of magnitude.

The change from nonpolar liquid media to the gas phase may well be expected to have a small effect on radical transfer reactions.[12] Thus the k_3 values determined in this work can serve as good estimates of the rate constants of the gas phase reaction between RSO_2 radicals and alkanes.

Comparison with the Gas Phase Photochemical Studies of the RH–SO_2 Systems. It is instructive to see whether the data obtained in this work could explain some of the observations made in the gas phase photolytic studies of the paraffin hydrocarbon-SO_2 systems. Assuming that the triplet state of sulfur dioxide, $^3SO_2$, is responsible for all the chemistry of the above systems,[4] sulfinic acids can be formed either by reaction 20 (route A) or by reactions 21 and 3 (route B). In order to estimate the relative importance of

$$^3SO_2 + RH \longrightarrow SO_2H + R \qquad (19)$$

$$R + SO_2H \longrightarrow RSO_2H \qquad (20)$$

$$R + SO_2 \longrightarrow RSO_2 \qquad (21)$$

$$RSO_2 + RH \longrightarrow RSO_2H + R \qquad (3)$$

those two routes several assumptions were made: (a) the concentrations of the R, RSO_2, and SO_2H radicals are roughly equal, (b) in the case of irradiation within the first allowed absorption band of SO_2 (2400-3200 Å) that is used in the photochemical studies, about 10% of the initially excited SO_2 molecules are converted into those of $^3SO_2$,[6] and (c) almost all of the quenching of $^3SO_2$ by alkanes higher than methane is chemical.[23] It can be shown that these assumptions lead to the following expression for the ratio of the rates of formation of sulfinic acids by the two routes

$$\frac{R_A}{R_B} = \frac{1}{3}\left[\frac{2\beta I_a k_{20}}{A}\right]^{1/2} / k_3[RH] \qquad (V)$$

where I_a is the absorbed light intensity in quanta/(l. sec), β denotes the fraction of initially excited molecules that are converted to $^3SO_2$ or another excited state of SO_2 that can abstract hydrogen from alkanes, $2k_{20}$ stands for the rate constant of biradical reactions, assumed to be equal for all the radicals in the system, and A is Avogadro's number.

Consider a typical photochemical system where $I_a = 10^{14}$ quanta/(l. sec) and assume that $\beta = 0.1$, $2k_{20} = 1 \times 10^{11}$ l./(mol sec), and $k_3 = 1.45 \times 10^2$ l./(mol sec), the value found for *n*-$BuSO_2$ in this work. According to expression V, R_A/R_B equals 0.3 under the above conditions and at an RH concentration of 10^{-2} l./mol. This value of R_A/R_B clearly indicates that both mechanism A and B can be responsible for the formation of sulfinic acids in the gas phase photolytic studies. Furthermore, hydrogen abstraction from alkanes by RSO_2 radicals can be expected to have an appreciable activation energy. Consequently, it is quite possible that with an increase of temperature, sulfinic acid formation shifts from the biradical to the hydrogen abstraction mechanism. In the systems in which this transition occurs a curvature of the Arrhenius plots of sulfinic acid formation should be observed. It should be noted that the square-root dependence of R_A/R_B on I_a, k_{20}, and β indicates that the conclusions reached by us are not limited by the values chosen for those parameters. It should also be pointed out that the increase of SO_2 concentration leads to the transition from the biradical to the hydrogen abstraction mechanism. This effect is due to the very efficient removal of R radicals by the reaction with SO_2 (reaction 21) that results in RSO_2 concentrations that are much higher than those of R. Thus it is quite possible that in systems where much SO_2 is present almost all the sulfinic acid will be formed by the hydrogen abstraction mechanism.

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Direct Synthesis of Fluorocarbon Peroxides. III. The Addition of Chloroperoxytrifluoromethane to Olefins

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Abstract: Chloroperoxytrifluoromethane, CF_3OOCl, undergoes addition reactions with olefins to yield trifluoromethylperoxy derivatives in high yield. The reactions are unidirectional and proceed by an electrophilic mechanism, in which the positive chlorine of CF_3OOCl adds to the carbon with the greatest number of hydrogens or the fewest fluorines. Reactions with C_2H_4, C_2F_4, C_2F_3Cl, CF_2CCl_2, CF_2CH_2, and *cis*-CFHCFH occur readily below 0°, whereas C_3F_6 and c-C_5F_8 were unreactive under all conditions tried. With *cis*-CFHCFH the reaction is stereospecific. The new peroxides exhibit high thermal stabilities and have been characterized by their physical properties and ir and nmr spectra.

Fluorocarbon peroxides can now be obtained in considerable number and variety by the direct addition of the CF_3OO group to suitable substrates. We have shown previously that the novel compounds, CF_3OOOCF_3,[1,2] CF_3OOH,[3-5] and CF_3OOF[6,7] are useful reagents for the direct synthesis of fluorocarbon peroxides, each having certain advantages in generating new peroxy derivatives. The reactions of CF_3OOH demonstrated thus far are polar in nature while those of CF_3OOOCF_3 and CF_3OOF are free radical. Chloroperoxytrifluoromethane, CF_3OOCl,[8] is also a potential reagent for the synthesis of CF_3OO derivatives. A brief, earlier report of some reactions of CF_3OOCl indicated, however, that reactions of CF_3OOCl probably proceeded by cleavage of the O-O bond. While it is likely that the O-O and O-Cl bonds in CF_3OOCl are of similar strengths, considering the utility of CF_3OCl[9,10] as a reagent for the synthesis of CF_3O derivatives and by analogy with the related compounds CF_3OOF and CF_3OF, it seemed reasonable to investigate CF_3OOCl as a potential source of new CF_3OO derivatives. In this paper we report the addition of CF_3OOCl to several olefins. In all cases involving ethylene and its chloro-fluoro derivatives, reaction proceeds readily at low temperatures to form peroxides which correspond to the simple addition of CF_3OOCl across the carbon-carbon double bond. Indeed, these reactions are quite analogous to the addition of CF_3OCl to olefins and are even more selective as no evidence was obtained for isomeric peroxides.

Experimental Section

General. All manipulations of volatile compounds were conducted in glass and stainless steel vacuum systems as previously described.[3] Quantities of reactants and products were measured by $n = PV/RT$, assuming ideal gas behavior or by direct weighing. Separation of volatile reaction mixtures was by trap-to-trap distillations and by glc using 49% halocarbon 11-21 polymer oil on acid washed Chromsorb P. Chromatography was carried out at appropriate temperatures between 22 and 45° using a 1 ft × 3/8 in. ss column for less volatile mixtures and a 10 ft × 3/8 in. ss column for mixtures boiling near or below room temperature. All glc separations employed gas injection.