

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

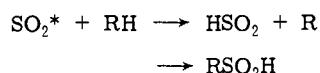
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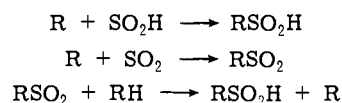
**Abstract:** The kinetics and mechanism of the  $\gamma$  radiation induced free radical chain decomposition of alkylsulfonyl chlorides ( $R'SO_2Cl$ ) dissolved in cyclohexane were studied at  $120^\circ$ . It was found that significant decomposition of  $R'SO_2$  radicals did not occur and that the 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 sulfonic acids. The following rate constants for hydrogen abstraction by  $R'SO_2$  radicals from cyclohexane were estimated at  $120^\circ$ :  $303 \pm 8$ ,  $245 \pm 8$ , and  $145 \pm 7$  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 sulfonic 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.<sup>1-4</sup> As was originally suggested by Dainton and Ivin<sup>1</sup> sulfonic 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.<sup>5-6</sup> 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 inser-



tion mechanism.<sup>4</sup> 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. Both routes lead to the formation of sulfonic acids.

Good and Thynne<sup>7</sup> determined the Arrhenius parameters for the addition of methyl and ethyl radicals to  $SO_2$ . Subsequent studies of Calvert, Slater, and Gall<sup>8</sup> 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.*<sup>9</sup> 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.<sup>10</sup> 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.<sup>11</sup> 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.<sup>12</sup> 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.<sup>13</sup>

## 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  $120 \pm 0.3^\circ$  and irradiated at a dose rate of  $1.56 \times 10^{15}$  eV/(ml sec). Gas chromatography was employed for product separation and analysis. Initially, Ucon and Silicon Gum Rubber SE-30 columns were used in unsuccessful attempts to separate the sulfonic acids. Since the sulfonic acids that were isolated up to now show thermal instability<sup>14,15</sup> it is quite possible that our failure was caused by the decomposition of the sulfonic acids on the gas-chromatographic column. Subsequent product analysis was carried out on a 6 ft by  $1/8$  in. stainless steel column, packed with Silicon Oil DC-200 on Chromosorb W, and temperature programmed from  $80$  to  $150^\circ$ . 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  $120^\circ$ . 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  $\pm 10\%$  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°<sup>a</sup>

| [R'SO <sub>2</sub> Cl],<br>mol/l. | Irr time,<br>min | G,<br>mol/100 eV | d[RCI]/dt<br>× 10 <sup>6</sup> ,<br>mol/(l. sec) | No. of<br>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' = <i>n</i> -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' = <i>n</i> -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              |

<sup>a</sup>  $G(\text{bicyclohexyl}) = 0.3 \pm 0.05$  in all experiments.

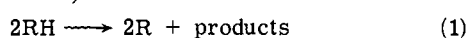
were not observed. In all the experiments the yield of bicyclohexyl was very low,  $G(\text{bicyclohexyl}) = 0.3 \pm 0.05$ .

In order to determine the rate of chlorine abstraction from alkylsulfonyl chlorides, solutions of C<sub>2</sub>Cl<sub>4</sub> and R'SO<sub>2</sub>Cl in cyclohexane were irradiated. The only detectable liquid products formed in these systems were chlorocyclohexane and trichlorovinylcyclohexane, RC<sub>2</sub>Cl<sub>3</sub>. A good material balance was observed in these experiments which are summarized in Table II.

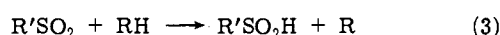
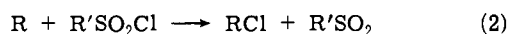
## Discussion

**Kinetic Scheme.** The  $G$  values of chlorocyclohexane formation observed by us in the RH-R'SO<sub>2</sub>Cl systems are considerably higher than the radiolytic yield of radicals in cyclohexane,  $G(\text{radicals}) = 5.7$ .<sup>16</sup> Hence, RCl and sulfinic acids have to be formed by a free radical chain mechanism described by the following reaction scheme.

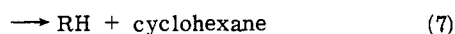
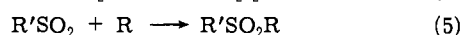
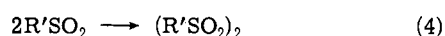
Initiation (schematic)



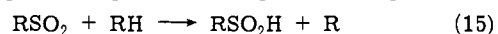
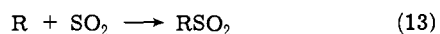
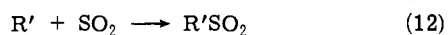
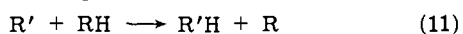
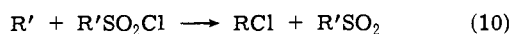
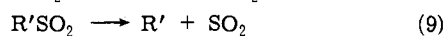
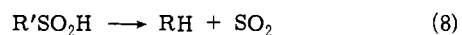
Propagation



Termination



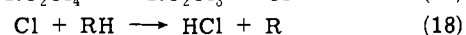
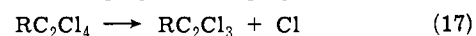
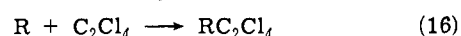
Additional reactions that could take place in the R'SO<sub>2</sub>Cl-RH system are



However, the occurrence of these reactions can be excluded

on the following grounds. In the liquid phase studies of the RH-SO<sub>2</sub> systems it has been qualitatively shown that the addition of alkyl radicals to SO<sub>2</sub> is a fast reaction.<sup>17,18</sup> Therefore, in the present system we would expect RSO<sub>2</sub>Cl 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<sub>2</sub>Cl-C<sub>2</sub>Cl<sub>4</sub> solutions in cyclohexane were carried out in order to determine the rate constant for the formation of the R'SO<sub>2</sub> radicals. In the RH-C<sub>2</sub>Cl<sub>4</sub> system, RC<sub>2</sub>Cl<sub>3</sub> is formed by a chain mechanism, whose propagation step is described by reactions 16-18. The rate



constant ratio is given by expression I provided that RCl and RC<sub>2</sub>Cl<sub>3</sub> are the only products formed by the reaction between the cyclohexyl radicals and the two solutes, as was

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

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  $4.18 \times 10^4$  l./mol sec for  $k_{16}$ . The latter value was calculated from the previously determined Arrhenius parameters of reaction 16.<sup>11</sup> It seems that the present data are not sufficient to establish whether the stability of the R'SO<sub>2</sub> 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]<sub>s</sub>, at given R'SO<sub>2</sub>Cl and C<sub>2</sub>Cl<sub>4</sub> concentrations. Values for [R]<sub>s</sub> calculated from expression II are given in Table II.

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

It is instructive to compare these values with the maximum steady state concentration, [R]<sub>max</sub>, of cyclohexyl radicals in the radiolysis of pure cyclohexane. [R]<sub>max</sub> is given by expression III where  $G[R]$ , the yield of radicals in cyclohex-

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

ane, is taken as 5.7<sup>16</sup> and  $\alpha$  is a factor that converts  $G$  values into rates of formation in units of molecules per liter second. At the applied dose rate  $\alpha$  is  $2.6 \times 10^{-8}$ . The assumption that the reaction between cyclohexyl radicals is diffusion controlled leads to a  $k_6 + k_7$  value of  $6.89 \times 10^9$  l./mol sec at 120°. This value was obtained by taking  $k_6 + k_7$  equal to  $1 \times 10^9$  l./mol sec at 25°<sup>19</sup> and the activation energy of diffusion in cyclohexane as equal to 4.54 kcal.<sup>20</sup> Upon substitution of the above estimated values into expression III [R]<sub>max</sub> is found to be  $3.9 \times 10^{-9}$  mol/l. Comparison of [R]<sub>max</sub> with the steady state concentrations of cyclohexyl radicals, given in Table II, indicates that in the presence of R'SO<sub>2</sub>Cl and C<sub>2</sub>Cl<sub>4</sub> the concentration of cyclohexyl radicals is drastically reduced.

From previous studies<sup>11</sup> of the RH-C<sub>2</sub>Cl<sub>4</sub> 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<sub>2</sub>Cl<sub>3</sub>) in Solutions of Tetrachloroethylene and Alkylsulfonyl Chlorides in Cyclohexane Irradiated at 120°<sup>a</sup>

| R'           | Irr time, min | [R'SO <sub>2</sub> Cl] <sub>0</sub> , mol/l. × 10 <sup>3</sup> | [C <sub>2</sub> Cl <sub>4</sub> ] <sub>0</sub> , mol/l. × 10 <sup>3</sup> | [RCl] <sub>f</sub> , mol/l. × 10 <sup>3</sup> | [RC <sub>2</sub> Cl <sub>3</sub> ] <sub>f</sub> , mol/l. × 10 <sup>4</sup> | -d[RCl]/d[R'SO <sub>2</sub> Cl] | [R] <sub>f</sub> <sup>b</sup> , mol/l. × 10 <sup>11</sup> |
|--------------|---------------|--|---|---|--|---------------------------------|---|
| 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  |
| <i>n</i> -Pr | 81            | 128.6  | 250   | 21.4  | 8.14   | 0.98                            | 1.60  |
|              | 32            | 123  | 200   | 12.4  | 5.63   | 1.09                            | 3.20  |
|              | 30            | 225  | 200   | 11.3  | 2.84   | 1.12                            | 1.72  |
| <i>n</i> -Bu | 63            | 225  | 200   | 22.3  | 6.36   | 0.98                            | 1.83  |
|              | 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  |

<sup>a</sup> [R'SO<sub>2</sub>Cl]<sub>0</sub> and [C<sub>2</sub>Cl<sub>4</sub>]<sub>0</sub> denote initial concentrations while [RC<sub>2</sub>Cl<sub>3</sub>]<sub>f</sub> and [RCl]<sub>f</sub> stand for final concentrations. <sup>b</sup> Calculated from eq II.

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

| R'           | <i>k</i> <sub>2</sub> / <i>k</i> <sub>16</sub> | <i>k</i> <sub>2</sub> <sup>a</sup> , l./(mol sec) × 10 <sup>-6</sup> | ( <i>k</i> <sub>3</sub> /2 <i>k</i> <sub>4</sub> ) <sup>1/2</sup> , (l./mol sec) <sup>1/2</sup> × 10 <sup>3</sup> | <i>k</i> <sub>3</sub> <sup>b</sup> , l./(mol sec) |
|--------------|--|--|---|---|
| Me           | 54.3 ± 2.1                                     | 2.27 ± 0.09  | 2.59 ± 0.07   | 303 ± 8   |
| <i>n</i> -Pr | 35.4 ± 2.6                                     | 1.48 ± 0.11  | 2.09 ± 0.07   | 245 ± 8   |
| <i>n</i> -Bu | 34.3 ± 0.7                                     | 1.43 ± 0.03  | 1.24 ± 0.06   | 145 ± 7   |

<sup>a</sup> *k*<sub>16</sub> at 120° taken as 4.18 × 10<sup>4</sup> l./(mol sec) calculated from data of ref 11. <sup>b</sup> 2*k*<sub>4</sub> 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<sub>2</sub> radicals comprise about 99% of the radicals. The importance of this conclusion lies in the fact that it is applicable also to the binary R'SO<sub>2</sub>Cl-RH systems.

**The Determination of the Rate Constant of Sulfonic Acid Formation. Reaction 3.** Based on the proposed reaction mechanism and the observed material balance the rate of formation of chlorocyclohexane, *R*<sub>RCl</sub>, and the rate of formation of the sulfonic acids, *R*<sub>R'SO<sub>2</sub>H</sub>, in the RH-R'SO<sub>2</sub>Cl systems have to be equal. Thus, in terms of the proposed reaction scheme, the rate of formation of the sulfonic acids should be given by expression IV. In the derivation of this

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

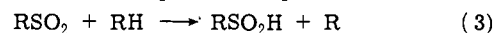
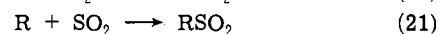
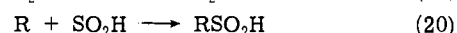
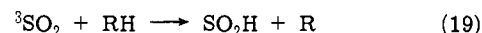
equation it has been assumed that practically all the radicals in the system are those of R'SO<sub>2</sub> as was shown in the previous section. Further experimental evidence supporting this assumption is provided by the low yields of bicyclohexyl found by us, *G*[R<sub>2</sub>] = 0.3 ± 0.05. This yield should be compared with *G*[R<sub>2</sub>] of 0.3, for bicyclohexyl that is formed in processes that are not affected by the presence of solutes,<sup>21</sup> and with *G*[R<sub>2</sub>] of 1.9, in pure cyclohexane that is independent of temperature.<sup>22</sup> 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*<sub>2</sub>/[2*k*<sub>4</sub>]<sup>1/2</sup> values that were calculated with the use of expression IV. In order to calculate from these ratios the value of *k*<sub>2</sub> it is necessary to know the value of *k*<sub>4</sub>. Unfortunately, the rate constants for the combination of alkylsulfonyl radicals have not been determined. In the derivation of the *k*<sub>2</sub> values of Table III it has been assumed that *k*<sub>4</sub> and *k*<sub>6</sub> + *k*<sub>7</sub> are equal. It is quite possible that the reaction between R'SO<sub>2</sub> radicals is considerably slower than the reaction between alkyl radicals. However, even if *k*<sub>4</sub> 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*<sub>3</sub> estimated by us would be accurate within an order of magni-

tude. 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*<sub>3</sub> is lower than *k*<sub>2</sub> 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.<sup>12</sup> Thus the *k*<sub>3</sub> values determined in this work can serve as good estimates of the rate constants of the gas phase reaction between RSO<sub>2</sub> radicals and alkanes.

**Comparison with the Gas Phase Photochemical Studies of the RH-SO<sub>2</sub> 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<sub>2</sub> systems. Assuming that the triplet state of sulfur dioxide, <sup>3</sup>SO<sub>2</sub>, is responsible for all the chemistry of the above systems,<sup>4</sup> sulfonic 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



those two routes several assumptions were made: (a) the concentrations of the R, RSO<sub>2</sub>, and SO<sub>2</sub>H radicals are roughly equal, (b) in the case of irradiation within the first allowed absorption band of SO<sub>2</sub> (2400–3200 Å) that is used in the photochemical studies, about 10% of the initially excited SO<sub>2</sub> molecules are converted into those of <sup>3</sup>SO<sub>2</sub>,<sup>6</sup> and (c) almost all of the quenching of <sup>3</sup>SO<sub>2</sub> by alkanes higher than methane is chemical.<sup>23</sup> It can be shown that these assumptions lead to the following expression for the ratio of the rates of formation of sulfonic acids by the two routes

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

where *I*<sub>a</sub> is the absorbed light intensity in quanta/(l. sec), β denotes the fraction of initially excited molecules that are converted to <sup>3</sup>SO<sub>2</sub> or another excited state of SO<sub>2</sub> that can abstract hydrogen from alkanes, 2*k*<sub>20</sub> 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*<sub>a</sub> = 10<sup>14</sup> quanta/(l. sec) and assume that β = 0.1, 2*k*<sub>20</sub> = 1 × 10<sup>11</sup> l./(mol sec), and *k*<sub>3</sub> = 1.45 × 10<sup>2</sup> l./(mol sec), the value found for *n*-BuSO<sub>2</sub> in this work. According to expression V, *R*<sub>A</sub>/*R*<sub>B</sub> equals 0.3 under the above conditions and at an RH concentration of 10<sup>-2</sup> l./mol. This value of *R*<sub>A</sub>/*R*<sub>B</sub> clearly indicates that both mechanism A and B can be responsible for the formation of sulfonic acids in the gas phase photolytic studies. Furthermore, hydrogen abstrac-

tion from alkanes by  $\text{RSO}_2$  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  $\beta$  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  $\text{SO}_2$  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  $\text{SO}_2$  (reaction 21) that results in  $\text{RSO}_2$  concentrations that are much higher than those of R. Thus it is quite possible that in systems where much  $\text{SO}_2$  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,  $\text{CF}_3\text{OOCl}$ , 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  $\text{CF}_3\text{OOCl}$  adds to the carbon with the greatest number of hydrogens or the fewest fluorines. Reactions with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_2\text{F}_3\text{Cl}$ ,  $\text{CF}_2\text{CCl}_2$ ,  $\text{CF}_2\text{CH}_2$ , and *cis*- $\text{CFHCFH}$  occur readily below  $0^\circ$ , whereas  $\text{C}_3\text{F}_6$  and *c*- $\text{C}_3\text{F}_8$  were unreactive under all conditions tried. With *cis*- $\text{CFHCFH}$  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  $\text{CF}_3\text{OO}$  group to suitable substrates. We have shown previously that the novel compounds,  $\text{CF}_3\text{OOOCF}_3$ ,<sup>1,2</sup>  $\text{CF}_3\text{OOH}$ ,<sup>3-5</sup> and  $\text{CF}_3\text{OOF}$ <sup>6,7</sup> are useful reagents for the direct synthesis of fluorocarbon peroxides, each having certain advantages in generating new peroxy derivatives. The reactions of  $\text{CF}_3\text{OOH}$  demonstrated thus far are polar in nature while those of  $\text{CF}_3\text{OOOCF}_3$  and  $\text{CF}_3\text{OOF}$  are free radical. Chloroperoxytrifluoromethane,  $\text{CF}_3\text{OOCl}$ ,<sup>8</sup> is also a potential reagent for the synthesis of  $\text{CF}_3\text{OO}$  derivatives. A brief, earlier report of some reactions of  $\text{CF}_3\text{OOCl}$  indicated, however, that reactions of  $\text{CF}_3\text{OOCl}$  probably proceeded by cleavage of the O—O bond. While it is likely that the O—O and O—Cl bonds in  $\text{CF}_3\text{OOCl}$  are of similar strengths, considering the utility of  $\text{CF}_3\text{OCl}$ ,<sup>9,10</sup> as a reagent for the synthesis of  $\text{CF}_3\text{O}$  derivatives and by analogy with the related compounds  $\text{CF}_3\text{OOF}$  and  $\text{CF}_3\text{OF}$ , it seemed reasonable to investigate  $\text{CF}_3\text{OOCl}$  as a potential source of new  $\text{CF}_3\text{OO}$  derivatives. In this paper we report the addi-

tion of  $\text{CF}_3\text{OOCl}$  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  $\text{CF}_3\text{OOCl}$  across the carbon-carbon double bond. Indeed, these reactions are quite analogous to the addition of  $\text{CF}_3\text{OCl}$  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.<sup>3</sup> 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 Chromosorb P. Chromatography was carried out at appropriate temperatures between 22 and  $45^\circ$  using a 1 ft  $\times$   $\frac{3}{8}$  in. ss column for less volatile mixtures and a 10 ft  $\times$   $\frac{3}{8}$  in. ss column for mixtures boiling near or below room temperature. All glc separations employed gas injection.