ethereal extracts were dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave 0.225 g (96%) of propiophenone.

General Procedure for Combined Alkylation and Cleavage Steps.—The alkylations were carried out as described above for the methylation of ω-(methylsulfinyl)acetophenone except that no attempt was made to crystallize or purify the crude alkylation product obtained upon removal of the solvent. This crude alkylation product was dissolved in 10% aqueous THF and reduced as described above for the preparation of propiophenone with the exception that the resulting ketones were extracted with pentane rather than with ether. The pentane solution was washed with water and dried over anhydrous magnesium sulfate, and the pentane was removed on a rotary evaporator. The crude ketones were distilled and the purity of the distillation product was checked by vapor phase chromatography.

Dialkylation. The Preparation of Isobutyrophenone. A. Two-Step Procedure.—ω-(Methylsulfinyl)acetophenone (5.0 g, 0.0275 mole) was methylated in DMF as described above using sodium hydride (0.66 g, 0.0275 mole) and methyl iodide (3.9 g, 0.0275 mole). After *ca.* 0.5-hr reaction time, the reaction mixture was transferred *via* syringe to a second reaction flask containing 0.66 g (0.0275 mole) of sodium hydride. When evolution of hydrogen ceased, the second equivalent of alkylating agent was added (in this case 3.9 g of methyl iodide) and the reaction mixture was stirred for *ca.* 45 min. Reduction with aluminum amalgam and distillation of the product yielded 2.21 g (54%) of isobutyrophenone, bp 68–72° (1 mm). A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol–ethyl acetate: mp 160–161° (lit.[4] mp 161–162°).

B. One-Step Procedure.—ω-(Methylsulfinyl)acetophenone (5.0 g, 0.0275 mole) was added to a slurry of sodium hydride (1.32 g, 0.055 mole) in 50 ml of DMF, and 3.9 g (0.0275 moles) of methyl iodide was added. After 0.5 hr an additional 3.9 g of methyl iodide in 50 ml of DMF was added and the reaction mixture was stirred for 40 min. Reduction and isolation were completed as described to yield 2.05 g (50%) of isobutyrophenone.

Propiophenone.—Propiophenone was prepared as outlined in the general procedure from 5.0 g (0.0275 moles) of ω-(methylsulfinyl)acetophenone. Distillation of the product yielded 2.37 g (64%) of propiophenone, bp 62–66° (1.5 mm), 2,4-dinitrophenylhydrazone mp 191–192° (lit.[5] mp 191°).

Butyrophenone.—Butyrophenone was prepared on the usual scale (0.0275 mole) as described in the general procedure using ethyl iodide as the alkylating agent and allowing the alkylation 1-hr reaction time. Distillation of the product gave 2.83 g (70%) of butyrophenone, bp 75–80° (1.5 mm), 2,4-dinitrophenylhydrazone mp 190–191° (lit.[4] mp 191–192°).

Valerophenone.—Valerophenone was prepared in the described manner except with *n*-propyl bromide as the alkylating agent and at reaction time of 22 hr at 55°. Distillation of the crude product gave 1.97 g (44%) of valerophenone, bp 82–86° (0.5 mm), 2,4-dinitrophenylhydrazone mp 164–165° (lit.[6] mp 165–166°).

3-Octanone.—3-Octanone was prepared by the general procedure described above except the reduction with aluminum amalgam required 1 hr in refluxing THF. Distillation of the crude product gave 62% of 3-octanone, bp 55–58° (1.5 mm), 2,4-dinitrophenylhydrazone mp 65–66° (lit.[7] mp 64–65°).

2-Methyl-3-octanone.—The procedure described for two-step dialkylation was followed in the preparation of this ketone. This procedure was modified to have a reduction time of 1 hr in refluxing THF. Distillation of the product gave 59% of ketone, bp 70–74° (1.5 mm), 2,4-dinitrophenylhydrazone mp 91–92° (lit.[8] mp 92.5°).

4-Nonanone.—The general procedure was followed, allowing an alkylation time of 1 hr and a reduction time of 1 hr in refluxing THF. Distillation gave 57% of product, bp 85–88° (2.0 mm).

4-Nonanone.—The same alkylation procedure was followed using DMSO as the solvent. The reaction mixture was poured into three times its volume of water and extracted with chloroform. The chloroform extracts were washed three times with water and the chloroform was evaporated. No attempt was made to isolate the intermediate keto sulfoxide. Reduction was completed as above. Methylsulfinylmethyl *n*-pentyl ketone (5 g, 0.0284 moles), sodium hydride (0.68 g, 0.0284 mole), and ethyl iodide (4.43 g, 0.0284 moles) yielded upon distillation 2.81 g (70%) of 4-nonanone.

Acknowledgment.—The authors are indebted to the National Science Foundation for Grant No. GP-4184 which partially supported this investigation.

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[5] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 363.

[6] J. Grundy, *J. Chem. Soc.*, 5087 (1957).

[7] J. H. Wotiz and J. S. Matthews, *J. Am. Chem. Soc.*, **74**, 2559 (1952).

[8] H. H. Morris and R. H. Young, Jr., *ibid.*, **77**, 6678 (1955).

A Study of Aliphatic Sulfonyl Compounds. VIII. The Thermal Decomposition of Trimethylmethanesulfonyl Chloride[1]

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Erroneous reports concerning trimethylmethanesulfonyl chloride and other tertiary aliphatic sulfonyl chlorides are discussed. Authentic trimethylmethanesulfonyl chloride has been synthesized and its instability examined, and conclusions regarding the mechanism of decomposition are presented. The extremely low activation energy and the complete ineffectiveness of free radical inhibitors and scavengers on the rates and product ratios for the vapor phase decomposition support the view that the reaction proceeds by either a cyclic, intramolecular mechanism or a radical nonchain mechanism which may be heterogeneous. The same conclusions are made for the mechanism of decomposition in solution, except for heterogeneity. The activation energies and A factors, while still remarkably low, are larger than the vapor phase counterparts.

The thermal vapor phase decomposition of some simple aliphatic primary and secondary sulfonyl chlorides and bromides has been studied carefully by Geiseler, *et al.*,[3a–c] In addition, Naumann[3d] studied the vapor phase decomposition of methanesulfonyl chloride. These studies leave little doubt that the

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[3] (a) G. Geiseler and H. Reinhardt, *Z. Physik. Chem.* (Frankfurt), **28**, 24 (1961); (b) G. Geiseler and R. Kuschmiers, *ibid.*, **28**, 33 (1961); (c) G. Geiseler and R. Kuschmiers, *ibid.*, **33**, 264 (1962); (d) E. Naumann, *Z. Physik. Chem.* (Leipzig), **211**, 332 (1959); (e) H. F. Herbrandson, W. S. Kelly, and J. Versnel, *J. Am. Chem. Soc.*, **80**, 3301 (1958); (f) F. Arndt and H. Scholz, *Ber.*, **66**, 1012 (1933); (g) A. Rieche and E. Naumann, *J. Prakt. Chem.*, (4) **9**, 108 (1959).

desulfination reaction in the gas phase proceeds by a radical chain process whereby each sulfonyl chloride molecule first undergoes homolysis at the sulfur-chlorine bond. The reaction takes place at a measurable rate generally at temperatures above 200°.

Although less definitive, studies of the liquid phase decomposition also indicate a free-radical mechanism is operative. For example, Herbrandson[3e] found racemization to occur when optically active 2-octanesulfonyl chloride was thermally decomposed. Arndt, *et al.*,[3f] reported that several sulfonyl chlorides have been used to initiate free radical reactions. Rieche and Naumann[3g] observed that easily hydrolyzed sulfonyl chlorides are more difficult to pyrolyze and concluded that homolytic cleavage of the carbon-sulfur bond is the rate-controlling step.

In view of the variety of sulfonyl chlorides used in these and other studies, a tertiary sulfonyl chloride would have been included for comparison had one been available. This paper is concerned with the results of such a study.

Although there are previous reports of the preparation of unsubstituted tertiary aliphatic sulfonyl chlorides, they are in error. Esayan[4] claimed to have prepared 2-methyl-2-butanesulfonyl chloride by oxidative chlorinolysis of what he thought was *t*-amylisothiuronium chloride. Instead, he apparently was working with methylisothiuronium chloride obtained on refluxing methanolic *t*-amyl chloride and thiourea, evidently unaware that this is characteristic behavior of tertiary halides,[5] and the product he obtained on oxidative chlorinolysis was simply methanesulfonyl chloride. Much earlier it had been shown that a sulfonyl chloride is not produced on oxidative chlorinolysis of *t*-butylisothiuronium salts.[6]

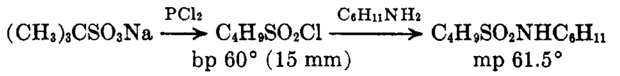
Although other sulfonyl chlorides can be prepared by oxidation of the sulfenyl chlorides,[7] including trichloromethanesulfonyl chloride[8] which is a sort of steric analog of trimethylmethanesulfonyl chloride, such attempts have failed to produce tertiary sulfonyl chlorides.[7a] It was considered that there might be some subtle barrier related to the inability to obtain *t*-butylsulfur trichloride[7a] from the sulfenyl chloride (although trichloromethylsulfur trichloride also cannot be prepared) and we unsuccessfully attempted to prepare the sulfonyl chloride by oxidative chlorinolysis of *t*-butyl trimethylmethanethiolsulfinate,[9] the latter being at the same stage of oxidation as the trichloride.

Helberger[10] reported having obtained the tertiary sulfonyl chlorides upon chlorosulfonylating isobutyl chloride, isopentyl chloride, and 4-chloro-2-methylpentane; however, this work also has been shown to be in error.[11] Already Asinger and Ebeneder[12a] had shown that no tertiary sulfonyl chloride results from chlorosulfonylation of isobutane; Scott and Heller[12b] likewise did not isolate a tertiary sulfonyl chloride on chlorosulfonylating 2,3-dimethylbutane. The only tertiary product was the chloride in each case.

Recently, however, we have been successful in producing tertiary sulfonyl chlorides on chlorosulfonylation of bicyclo[2.2.2]octane[13] and adamantane[9] as substrates, although separation from the secondary isomer in either case was not effected. In order to account for this remarkable behavior of the bicyclic hydrocarbons it is necessary to understand the mechanism of chlorosulfonylation. This reaction has been shown to be a radical chain process in which the hydrocarbon free radical forms the conjugate sulfonyl free radical.[14] Probably this is an equilibrium reaction in which an acyclic tertiary free radical is thermodynamically more stable than the neopentyloid sulfonyl free radical. The bridgehead sulfonyl halides are successfully prepared this way evidently because of the much greater instability of the bridgehead free radical compared with acyclic ones and the resulting more favorable position of equilibrium between it and its conjugate sulfonyl free radical.

Although we were unable to separate the two isomeric sulfonyl chlorides evidently obtained on chlorosulfonylating each *sym*-bicyclooctane and adamantane, derivatization with ammonia of the residue from long deposition of the product yielded from the former only the known 2-bicyclo[2.2.2]octanesulfonamide, mp 132–133°.[13,15] Evidently 2-adamantanesulfonamide, mp 208.5–209.5°, was obtained as the sole product from the mixture of isomers in the latter case.[9] It is our belief that a mixture of the secondary and tertiary isomers was obtained on chlorosulfonylating each of these hydrocarbons and that the tertiary ones are unstable and do not give sulfonamides.

Asinger[12a] claimed to have prepared trimethylmethanesulfonyl chloride by the action of phosphorus pentachloride on the corresponding acid. He obtained a liquid, evidently of normal stability, from which a solid derivative, mp 61.5°, presumed to be an amide was prepared with cyclohexylamine.



$$(CH_3)_3CSO_3Na \xrightarrow{PCl_2} \underset{\text{bp } 60^\circ \text{ (15 mm)}}{C_4H_9SO_2Cl} \xrightarrow{C_6H_{11}NH_2} \underset{\text{mp } 61.5^\circ}{C_4H_9SO_2NHC_6H_{11}}$$

Attempts by Hunt[16] and others in these laboratories[17] to repeat this work failed, even after following a later suggestion[18] to use very low temperatures.

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(17) (a) M. K. Frye, Thesis, University of Alabama, 1951; (b) H. L. McLeod, Dissertation, University of Alabama, 1956.

(18) F. Asinger, private communication, 1956. In this it was disclosed that others had experienced difficulty in repeating the work and it was reported that the homologous 2-methyl-2-butanesulfonyl chloride had been prepared in similar manner.

In view of the facts that trichloromethanesulfonyl chloride cannot be prepared from the sulfonic acid[19] whereas trifluoromethanesulfonyl chloride can[7b,20] and both trichloromethanesulfinyl chloride[21] and trimethylmethanesulfinyl chloride[22] are readily obtained from the sulfinic acids, we believe that tertiary sulfonyl chlorides cannot be prepared from the sulfonic acids for steric reasons.

While primary or secondary sulfonyl chlorides react with amines to form sulfonamides by an elimination–addition sequence involving a reactive sulfene intermediate,[23] a sulfonamide could be prepared from a tertiary sulfonyl chloride only by nucleophilic displacement of the halogen. Primary or secondary sulfonyl chlorides also undergo nucleophilic displacement of halogen with weaker bases such as water or alcohols,[23c] and steric hindrance to this has been demonstrated.[12b,24,25] Consequently sulfonamide formation from tertiary sulfonyl chlorides[26] would be expected to be a remarkably slow process. It is assumed that a normal reaction time was involved in the case reported by Asinger since no comment was made to the contrary. This raised doubt that he actually had the tertiary sulfonyl chloride. In fact, since Geiseler referred[25] to unpublished work with Asinger showing that the neutral hydrolysis of tertiary sulfonyl chlorides is much slower than that of secondary ones, it is questionable that he was referring to the same compound reported by Asinger.

Furthermore, trichloromethanesulfonyl chloride is sterically analogous to trimethylmethanesulfonyl chloride and does not give sulfonamides on reaction with amines,[19,27] while trifluoromethanesulfonyl chloride does[20] and both trichloromethanesulfinyl chloride[21] and trimethylmethanesulfinyl chloride[28] give the sulfinamides. Steric considerations, therefore, suggest that trimethylmethanesulfonyl chloride should not give sulfonamides, contrary to the Asinger report.

From structural considerations one would expect trimethylmethanesulfonyl chloride to have a relatively high melting point and not to be a liquid as reported by Asinger. Thus many, although not all, sterically analogous substances are solids, such as trimethylmethanesulfonic acid (mp 100°),[29a] trichloromethanesulfonyl chloride (mp 140.5°, 143°),[29b] hexamethylethane (mp 100.7°),[29c] triptyl chloride (mp 136°),[29d] hexachloroethane (mp 188.7°),[29e] and chloretone (mp 97°).[29f]

Indeed, we have shown unequivocally that the derivative obtained by Asinger is not the amide of trimethylmethanesulfonic acid by preparing the authentic material both by oxidation of the sulfenamide derived

$$(t\text{-BuS})_2 \xrightarrow[\text{isopentane}]{\mathrm{Cl_2}} t\text{-BuSCl} \xrightarrow{\text{cyHxNH}_2} t\text{-BuSNHcyHx} \xrightarrow[\mathrm{Me_2CO}]{\mathrm{KMnO_4}} t\text{-BuSO}_2\text{NHcyHX}$$

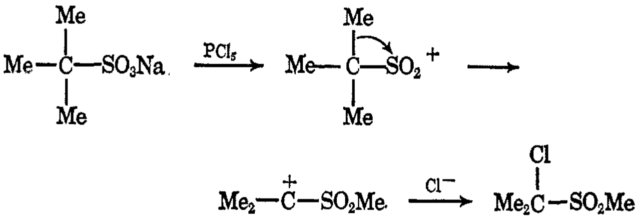
mp 118–119°

from the sulfenyl chloride and oxidation of the sulfinamide[28] derived from the Grignard-based sulfinyl chloride.

$$t\text{-BuMgCl} \xrightarrow[\text{2. NH}_4\text{Cl, HOH}]{\text{1. SO}_2} t\text{-BuSOOH} \xrightarrow{\mathrm{SOCl_2}} t\text{-BuSOCl} \xrightarrow{\text{cyHxNH}_2} t\text{-BuSONHcyHx} \xrightarrow[\mathrm{Me_2CO}]{\mathrm{KMnO_4}} t\text{-BuSO}_2\text{NHcyHx}$$

mp 118–119°

Evidently the substance prepared by Asinger is not trimethylmethanesulfonyl chloride. No satisfactory answer is at hand to account for his product since no isomeric sulfonyl chloride, chloro sulfone, or chloro sulfite which might reasonably be expected has similar properties to his. While an α-chloro sulfone might be anticipated *via* a retropinacoloid rearrangement of a B-strained sulfonylium ion (see the scheme below),



$$\mathrm{Me_3C{-}SO_3Na} \xrightarrow{\mathrm{PCl_5}} \mathrm{Me_3C{-}SO_2^+} \longrightarrow \mathrm{Me_2\overset{+}{C}{-}SO_2Me} \xrightarrow{\mathrm{Cl^-}} \mathrm{Me_2\overset{Cl}{C}{-}SO_2Me}$$

the bulky sulfo group should render the compound essentially inert to nucleophilic displacement of the halogen.[30] Although in at least one instance a β-chloro sulfone has been mistaken for a sulfonyl chloride,[31] no reasonable mechanism is apparent whereby one could be formed here.

Hunt[16] and we[17a] have prepared a substance meeting the expected criteria for trimethylmethanesulfonyl chloride in 11% yield based on *t*-butyl chloride by means of the Cherbuliez reaction[32a] on addition of ethereal sulfuryl chloride to *t*-butylmagnesium chloride in cold ether solution. The yield is doubled (26%)[32b] on using the Scott modification[32c] of chlorination of the sulfinated Grignard reagent. It is doubled again (50%) on adding neat sulfuryl chloride to the free sulfinic acid. In the last case it also is obtained in a

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[19] G. McGowan, *J. Prakt. Chem.*, [2] **30**, 280 (1884).

[20] T. J. Brice and P. W. Trott, U. S. Patent 2,732,398 (1956); *Chem. Abstr.*, **50**, 13982 (1956).

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[25] G. Geiseler, P. Hermann, K. H. Reps, and R. Wüstner, *Z. Phys. Chem.* (Leipzig), **229**, 185 (1962).

[26] Obviously the steric requirement for nucleophilic displacement of halogen from an aromatic sulfonyl chloride would be somewhat less than that of a secondary one.

[27] (a) O. Loew, *Z. Chem.*, **12**, 82 (1869); (b) G. McGowan, *J. Prakt. Chem.*, [2] **29**, 138 (1884); (c) M. Battegay and W. Kern, *Bull. Soc. Chim. France*, [4] **41**, 34 (1927);

[28] H. E. Johnson, Thesis, The University of Mississippi, 1966.

[29] (a) H. J. Backer and P. L. Stedehouder, *Rec. Trav. Chim.*, **52**, 437 (1933); (b) M. S. Schechter and H. L. Haller, *J. Am. Chem. Soc.*, **63**, 1764 (1941); F. A. Drahowzal, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 371; (c) G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro, *J. Am. Chem. Soc.*, **66**, 1389 (1944); (d) H. A. Butlerow, *Ann.*, **177**, 176 (1875); (e) W. Staedel, *Ber.*, **11**, 1735 (1878); (f) C. Willgerodt, *ibid.*, **14**, 2451 (1881).

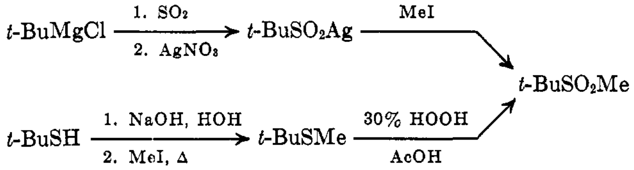
[30] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5164 (1951).

[31] M. S. Kharasch and A. F. Zavist, *ibid.*, **70**, 3526 (1948); **73**, 964 (1951).

[32] (a) E. Cherbuliez and O. Schnauder, *Helv. Chim. Acta*, **6**, 249 (1923). (b) J. M. Lyster, undergraduate research, University of Alabama, 1961; (c) R. B. Scott, Jr., J. B. Gayle, M. S. Heller, and R. E. Lutz, *J. Org. Chem.*, **20**, 1165 (1955).

much more nearly pure form. Recently it also has been prepared by oxidation of the sulfinyl chloride with chlorine water or permanganic acid.[28]

There can be no question that a carbon–sulfur bond is formed on sulfination of the Grignard reagent. Rheinboldt[33a] prepared what he considered to be methyl *t*-butyl sulfone by alkylation of the silver salt derived from the sulfinated product and we prepared the identical sulfone by oxidizing the corresponding sulfide.[33b]



The possibility of a hypochlorite-like structure, RS(O)OCl, which was considered only because of the disagreement with the Asinger report, is ruled out by the strong absorbance in the infrared at 1145 cm^{-1}, since strong absorbance in the 1130–1145-cm^{-1} region has been shown to be diagnostic for other tertiary sulfonyl compounds,[11c] including the ethyl sulfonate derived from the same sulfonic acid Asinger reported having used, and the N-cyclohexylsulfonamide mentioned earlier as having been prepared by oxidation of either the sulfenamide or the sulfinamide. This is a particularly significant red shift in the symmetrical SO_2 stretching frequency from the 1165–1180-cm^{-1} region observed for a large number of primary and secondary halides of various kinds. There was absorbance also at 1360 cm^{-1}, a characteristic of aliphatic sulfonyl chlorides assigned to asymmetrical SO_2 stretch. Assignments are given in Table I for the principal absorbance bands in the spectrum. Further evidence against the hypochlorite structure already mentioned is oxidation of the sulfinyl chloride[28] which had been prepared by allowing the sulfinic acid to react with thionyl chloride.

Trimethylmethanesulfonyl chloride is not at all like the compound reported by Asinger. It is a solid melting at 95.0–95.5°, whereas his was a liquid. Unlike primary and secondary sulfonyl chlorides, it is not stable at ambient temperatures, decomposing with a half-life of about 34 hr at 35°.[34,35] Evidently that substance which Asinger prepared was stable since it was distilled at 60° (15 mm). The authentic tertiary sulfonyl chloride reacts vigorously with cyclohexylamine or with benzylamine but, instead of producing a sulfonamide as Asinger's compound was reported to have done, only *t*-butyl chloride and the amine complex of sulfur dioxide were obtained.[16,17b]

Table I

Principal Infrared Absorption of Trimethylmethanesulfonyl Chloride in Carbon Tetrachloride[a]

Absorbance		Assignment	
$\bar{\nu}$, cm^{-1}	Intensity	Bond	Mode
645	s	C–S	st
670	w, sh	?	?
1022	w	CH_3	rk
1145	vs	SO_2	s, st
1197	m	*t*-Bu	bd
1360	vs	SO_2	a, st
1378	s, sh	*t*-Bu	?
1402	w	*t*-Bu	?
1463	m	CH_3	wg
1475	m	CH_3	tw
2490	m	CH_3	a, st
2998	s	CH_3	a, s, st

[a] Intensity: s = strong, w = weak, m = moderate, v = very, sh = shoulder. Mode: bd = bend, st = stretch, rk = rock, wg = wag, tw = twist, a = asymmetric, s = symmetric.

Hunt observed[16] that the authentic tertiary sulfonyl chloride decomposed to *t*-butyl chloride and sulfur dioxide within 2 min after addition of phosphorus pentachloride at room temperature.

In view of the quite different chemical and physical behavior from that of primary and secondary sulfonyl chlorides, a different decomposition mechanism was thought to be possible for tertiary sulfonyl chlorides. Accordingly, a kinetic investigation was begun of the decomposition in particular of trimethylmethanesulfonyl chloride[36] and, to a very limited extent, owing to our inability to separate the tertiary isomers, of adamantane-[9] and *sym*-bicyclooctanesulfonyl[13] chlorides.

As the solid, in solution, and in the vapor phase, trimethylmethanesulfonyl chloride decomposes to *t*-butyl chloride, isobutylene, sulfur dioxide, and hydrogen chloride. In Table II are given the rate constants and Arrhenius parameters for the decomposition of it neat in comparison with the decomposition of the tertiary sulfonyl chlorides of adamantane and *sym*-bicyclooctane, but with them in the presence of their secondary isomers (which presumably did not materially decompose).

Although, as shown later, decomposition of trimethylmethanesulfonyl chloride probably does not proceed

Table II

Comparison of Rate Constants for Decomposition of Some Tertiary Sulfonyl Chlorides in Condensed Phases

Sulfonyl chloride	Temp, °C	10^7k, sec^{-1}	E_a, kcal	log *A*, sec^{-1}	Phase
Trimethylmethane-	25	8.05[a]	20.8	9.17	Solid
	35	58.0[a]			
	50	320[a]			
	65	1200[b]			
1-Adamantane-[c]	22.5	40.0	10.8	2.35	Liquid[d]
	34.9	52.7			
	50.0	103			
	62.5	205			
1-Bicyclo[2.2.2]-octane-[b,e]	90.0	141	26.2	10.93	Liquid[d]
	110.0	255			
	115.0	1570			

[a] M. K. Frye, Thesis, University of Alabama, 1951. Measured by following loss in weight after periodic removal of decomposition products by evacuation for a short time. [b] Measured by following rate of SO_2 evolution by gas chromatography. [c] R. T. van Aller, Thesis, University of Alabama, 1963. Measured by following loss in weight after periodic removal of any dissolved SO_2. [d] Mixture of tertiary and secondary isomers. [e] D. Kinzer, Thesis, University of Alabama, 1964.

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(33) (a) H. Rheinboldt, F. Mott and E. Motzkus, *J. Prakt. Chem.*, **134**, 257 (1932); (b) J. D. Johnson, undergraduate research, University of Alabama, 1961.

(34) Hunt[16] observed a half-life of 31 hr at 25°.

(35) In Geiserler's reference[25] to unpublished work by him and Asinger, mention was made of the thermal instability of tertiary sulfonyl chlorides. As pointed out earlier, it is questionable whether the work was with the compound reported by Asinger.

(36) E. L. Brockelbank, Thesis, University of Alabama, 1964.

TABLE III

RATE CONSTANTS FOR THE DECOMPOSITION OF TRIMETHYLMETHANESULFONYL CHLORIDE IN HYDROCARBON SOLUTIONS

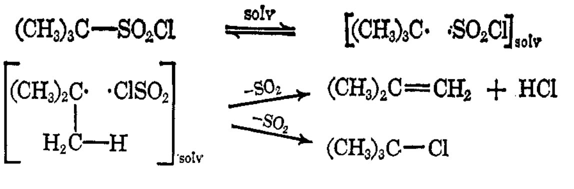
Solvent	Initial concn, M	Temp, °C	10^6k, sec^{-1}	E_a, kcal	log A, sec^{-1}	ΔS^*, eu	ΔF^*, kcal
n-Hexane	0.2	65	5.99 ± 0.43				
n-Heptane	0.2	65	6.29 ± 0.17				
n-Octane				22.3 ± 0.9	9.03	−19.0	28.0
	0.2	65	4.25 ± 0.12				
		85	30.6 ± 0.6				
		95	41.0 ± 0.4				
n-Tetradecane				23.8 ± 0.3	9.97	−15.2	28.3
	2.68	65[a]	3.55 ± 0.02				
		85[a]	26.5 ± 0.2				
		95[a]	63.7 ± 1.7				
	0.204	65	3.59 ± 0.04				
		75	9.62 ± 0.09				
o,p-Xylene[b]				38.6 ± 0.8	18.35	23.1	29.0
	0.2	65	1.12 ± 0.11				
		75	6.70 ± 0.13				
		85	25.3 ± 1.1				

[a] Oxygen scavenger added as the sweeping gas. [b] Commercial mixture of isomers.

by a free-radical mechanism, stability of the three tertiary sulfonyl chlorides is in the reverse order to the stability of the tertiary free radicals, which is *t*-Bu > 1-Adam > 1-*sym*-BicyOct. This is in agreement with the view that chlorosulfonylation is unsuccessful for the preparation of a sulfonyl chloride when the hydrocarbon free radical is more stable than its conjugate sulfonyl free radical, and one would not expect to be able to prepare acyclic tertiary, benzylic, or allylic sulfonyl chlorides in this way.

The rate of decomposition of trimethylmethanesulfonyl chloride is markedly slower when dissolved in a hydrocarbon than in the absence of a solvent; however, this is not a concentration effect. Changing the concentration in tetradecane only brought about a change in the ratio of *t*-butyl chloride to isobutylene, probably resulting from addition of hydrogen chloride to the olefin. In fact, on decomposition in a sealed tube, *t*-butyl chloride and sulfur dioxide are the only products. In Table III are given the rate constants and Arrhenius parameters for the decomposition of trimethylmethanesulfonyl chloride in various hydrocarbon solvents. The kinetic data show that the rate of decomposition is solvent dependent, decreasing with increasing chain length of the paraffin solvents heptane through tetradecane and even more in xylene solution.

Supposing primary cleavage of the tertiary carbon–sulfur bond, the Franck–Rabinowitsch effect might be expected to account for the solvent dependency. This seems to be in agreement with the low A factor if the solvent cage were considered to be highly ordered enough to restrict the freedom of orientation of the chlorosulfonyl–chlorosulfite hybrid radical: the greater the restriction, the greater the proportion of internal return with reformation of the sulfonyl chloride. This may be pictured as shown in the scheme below.



However, the solvent dependency cannot be accounted for on a basis of increased hindrance to diffusion of free radicals since there was no concentration effect on the rate of decomposition in tetradecane when concentration of the sulfonyl chloride was changed by a factor of more than 13.

The effect of solvent internal pressure on rates of nonionic reaction in nonpolar media has been observed and studied by several investigators.[37] Such an effect may be operative here and would also account for the large difference between these rates and the rate in the vapor phase. Possibly a study of the decomposition in a larger variety of solvents having greater differences in internal pressure will help answer this question.

The results of adding free radical scavengers to the decomposing sulfonyl chloride rule out the possibility of a radical chain process. For example, decomposition when starting with a 1:1 molar ratio of the sulfonyl chloride and bromotrichloromethane produces only the normal decomposition products; if the reaction were free radical in nature, *t*-butyl bromide and carbon tetrachloride would be likely products.[38] Also, oxygen has no effect on the rate of decomposition in *n*-tetradecane at 65° when bubbled into the solution.

Decomposition of 0.58 M solution of the sulfonyl chloride in toluene likewise produces only the normal decomposition products. Toluene has been shown to be an effective radical trap[39] and products such as chlorotoluenes and *sym*-diphenylethane should have been produced in the presence of free radicals.

The rate of formation of free radicals in solution may be conveniently measured also on using iodine[40] by

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[37] (a) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963); (b) J. Halpern, G. W. Brady, and C. A. Winkler, *Can. J. Res.*, **28B**, 140 (1950); (c) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, **68**, 651 (1964); (d) a similar effect was observed in the decomposition of diacetyl peroxide; W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

[38] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

[39] A. Rembaum and M. Szwarc, *ibid.*, **76**, 5975 (1954); M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

[40] M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955); J. C. Roy, J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 519 (1956); G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

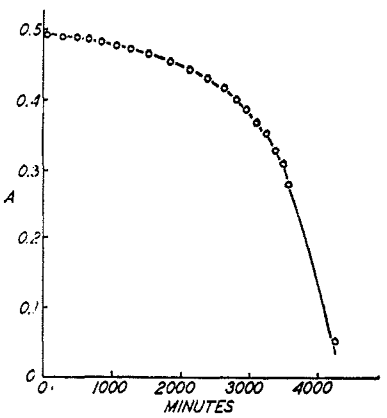

Figure 1.—Absorbance of iodine in solutions of trimethylmethanesulfonyl chloride in *n*-heptane during decomposition at 65° under the influence of light.

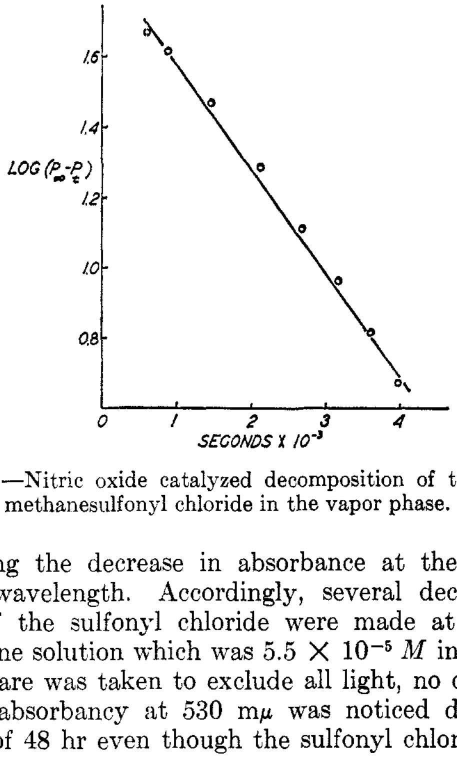

Figure 2.—Nitric oxide catalyzed decomposition of trimethylmethanesulfonyl chloride in the vapor phase.

observing the decrease in absorbance at the appropriate wavelength. Accordingly, several decompositions of the sulfonyl chloride were made at 65° in *n*-heptane solution which was 5.5×10^{-5} *M* in iodine. When care was taken to exclude all light, no decrease in the absorbancy at 530 mμ was noticed during a period of 48 hr even though the sulfonyl chloride was largely decomposed, but, when the black reactor was replaced with a transparent one illuminated with a 250-w sunlamp, the absorbance decreased with time as shown in Figure 1.

This photochemical reaction is probably due to an induced reaction caused by photolysis of iodine.[41] Presumably, the iodine atoms thus produced could then react with sulfonyl chloride molecules.

$$I_2 \overset{h\nu}{\rightleftharpoons} 2I\cdot$$

$$I\cdot + t\text{-BuSO}_2\text{Cl} \longrightarrow t\text{-BuSO}_2\cdot + \text{ICl}$$

It might be argued that the iodine is decolorized by radicals produced by photolysis of the sulfonyl chloride.

$$t\text{-BuSO}_2\text{Cl} \xrightarrow{h\nu} t\text{-Bu}\cdot + \text{SO}_2 + \text{Cl}\cdot$$

$$\text{Cl}\cdot + I_2 \longrightarrow \text{ICl} + I\cdot$$

However, only a small amount of decomposition was noted when a toluene solution of the sulfonyl chloride was irridated for 74 hr at 30°, and this was believed to be thermal. In addition, no products characteristic of the solvent were observed.

The strong curvature in Figure 1 may be the result of competitive reactions with the atomic iodine, *e.g.*, by *t*-butyl chloride.

These results rule out a radical chain process as a plausible mechanism of decomposition and, coupled with the low activation entropy values, leave little doubt that the decomposition involves a cyclic transition state.[42] In the vapor phase, the product ratio of hydrogen chloride and isobutylene to *t*-butyl chloride is 2:1 over the entire temperature range employed. The addition of hydrogen chloride to isobutylene in the vapor phase at the concentrations and temperatures used is slow enough to be negligible.[43]

A radical chain process can also be discounted for the vapor phase decomposition. The rate constants shown in Table IV obtained when toluene (50 mm) and when oxygen (20 mm) were added to the decomposing sulfonyl chloride in the vapor phase at 105° are not significantly different.

Table IV

Rate Constants and Arrhenius Parameters for the Vapor Phase Decomposition of Trimethylmethanesulfonyl Chloride[a]

Temp, °C	10^5k, sec^{-1}	Remarks
90.0	5.50 ± 0.01	
90.0	4.82 ± 0.06	
95.0	6.61 ± 0.08	
95.0	6.03 ± 0.09	
100.0	9.36 ± 0.15	
110.1	16.2 ± 0.06	
110.0	16.0 ± 0.07	
115.0	19.0 ± 0.20	
105.0	11.0	Calculated
105.0	11.0 ± 0.12	50 mm toluene
105.0	10.3 ± 0.20	20 mm O_2
105.0	71.4[b]	20 mm NO

[a] $E_a = 15.3 \pm 0.8$ kcal; $A = (7.6 \pm 3.0) \times 10^4$ sec^{-1}; $\Delta H^* = 14.5 \pm 0.8$ kcal; $\Delta S^* = -38.6 \pm 2.2$ eu; $\Delta F^* = 26.0 \pm 0.8$ kcal. [b] Approximate, owing to plot curvature.

Nitric oxide, the classical inhibitor,[44] instead caused the decomposition rate to be increased sixfold, and, moreover, apparently catalyzed the hydrogen chloride addition to isobutylene since the final product analysis after a relatively long time showed a decrease in isobutylene concentration and an increase in *t*-butyl chloride concentration. The plot shows a strong curvature, the rate constant increasing with time, indicating that one of the products, possibly sulfur dioxide, enters into a catalyzed decomposition with the nitric oxide. This is apparent from Figure 2. In any event, no inhibition occurred with nitric oxide as the additive.

Further evidence that the vapor phase decomposition proceeds other than by a radical chain process is provided by the fact that no isobutyl chloride is found in

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[41] F. W. Lampfe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954); D. J. Sibbett and R M. Noyes, *ibid.*, **75**, 761 (1953).

[42] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 181, 182; J. Hine, "Physical Organic Chemistry," The McGraw-Hill Book Co., New York, N. Y., 1962, pp 507–515.

[43] G. B. Kistiakowsky and C. H. Stauffer, *J. Am. Chem. Soc.*, **59**, 165 (1937).

[44] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 107; K. J. Laidler, "Chemical Kinetics," The McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 393–396.

the reaction products. A free-radical decomposition similar to that observed for primary and secondary sulfonyl chlorides would generate chlorine atoms which would then add to isobutylene forming isobutyl chloride.[45] However, a homolytic nonchain process cannot be ruled out by these facts.

Rate constants and transition state parameters for the vapor phase decomposition are shown in Table IV and the Arrhenius plot in Figure 3. The rate constant expressed as a function of temperature is given in the following equation.

$$k = (7.6 \pm 3.0) \times 10^4 e^{-15{,}300 \pm 800 \text{ cal}/RT} \text{ sec}^{-1}$$

The extremely low A factor, corresponding to the very low activation entropy (−38.6 eu), suggests that the rate-determining step proceeds through a very highly ordered activated complex. Mention has already been made of the constancy of products ratio in the vapor phase at different temperatures. This same ratio has also been observed in the decomposition of the solid sulfonyl chloride at 65° and even when the decomposition was carried out very rapidly in the heated port of the gas chromatograph at 320° on injection of various solutions of the sulfonyl chloride. Available data on covalent bond lengths and angles[46] give a value of about 2.0 A between centers of the hydrogen and chlorine atoms in the trimethylmethanesulfonyl chloride molecule. Normal bending vibrations will decrease this distance; *e.g.*, a deformation of the carbon–sulfur–chlorine angle by as little as 20° leads to a value of about 1.4 A, which is somewhat greater than the actual bond length of 1.275 A for hydrogen chloride.[46] Because of this proximity, relatively little activation energy should be necessary for the molecule to attain the cyclic transition state.[41] The facts suggest that *t*-butyl chloride and the elimination products arise from a common transition state which may be pictured[47] as in Figure 4.

An alternative explanation for the constant ratio of products with temperature variation is that the energy of activations and frequency factors for elimination and internal return reactions are very nearly equal. This, of course, is not very likely.

Both the low entropy and energy of activation may equally well be accounted for in terms of a surface-catalyzed reaction. It has been claimed that A factors below 10^5 sec^{-1} indicate heterogeneity.[48]

Geiseler[3a] found that toluene increasingly inhibits decomposition of 1- and 2-propanesulfonyl chlorides as the decomposition temperature is lowered. He also found heterogeneity in the lower temperature regions below 330° for 1-propanesulfonyl chloride, the Arrhenius plot showing a strong curvature at the lower temperatures. The Arrhenius plot for the decomposition of ethanesulfonyl chloride also shows a strong curvature in the lower temperature region, the activation energy decreasing to about 15 kcal.[3b] If this value is substituted into the Arrhenius equation for ethanesulfonyl chloride along with the rate constant at the lowest temperature, about 1×10^{-4} sec^{-1} as taken from the Geiseler graph, the A factor is calculated to be about 9×10^1 sec^{-1}, an extremely low value. In addition, the decomposition of methanesulfonyl chloride was found to be heterogeneous over the entire range of temperature studied, E_a being 24 kcal and log A being 4.92.

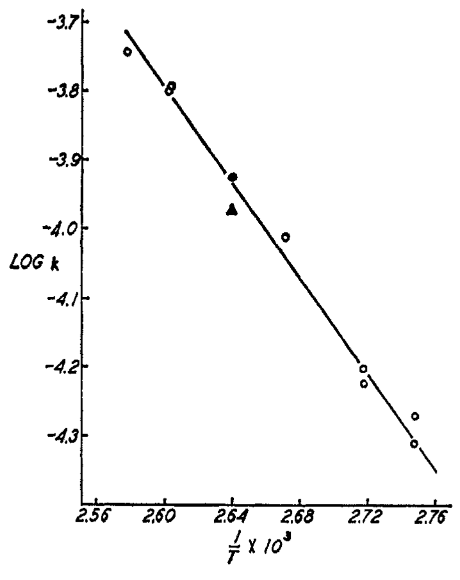

Figure 3.—Arrhenius plot for the vapor phase decomposition of trimethylmethanesulfonyl chloride. Oxygen as diluent, ▲; toluene as diluent, ●.

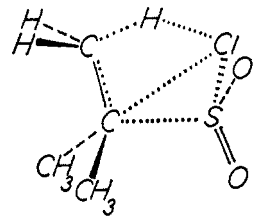

Figure 4.—Transition state for intramolecular decomposition of trimethylmethanesulfonyl chloride.

The vapor phase decomposition of trimethylmethanesulfonyl chloride appears to have a wall effect, indicating heterogeneity.[49] Washing the flask with nitric acid after each of the first few experiments caused rate constants to be as much as three times greater than when the flask was "aged" by repeated experiments without cleaning.

If one assumes the decomposition of trimethylmethanesulfonyl chloride to be heterogeneous and free radical, it must proceed without a chain-induced decomposition step or steps, in view of the constancy of the rate constant and the products ratio when toluene and oxygen are present. A mechanism consistent with these observations follows.

$$t\text{-BuSO}_2\text{Cl} + \text{W}^* \xrightarrow{k_1} t\text{-Bu}\cdot + \text{SO}_2 + \text{Cl}\cdot + \text{W} \quad (1)$$

$$t\text{-Bu}\cdot + \text{Cl}\cdot + \text{W} \xrightarrow{k_2} t\text{-BuCl} + \text{W}^* \quad (2)$$

$$t\text{-Bu}\cdot + \text{W} \xrightarrow{k_3} \text{olefin} + \text{H}\cdot + \text{W}^* \quad (3)$$

$$\text{H}\cdot + \text{Cl}\cdot + \text{W} \xrightarrow{k_4} \text{HCl} + \text{W}^* \quad (4)$$

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[45] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 2767 (1948); G. G. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950); F. R. Mayo, *ibid.*, **76**, 5392 (1954).

[46] "Handbook of Chemistry and Physics," R. C. Weast, Ed., 45 ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, pp F-90 to F-93.

[47] The concept of two products resulting from the same transition state is not new. See, for example, J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

[48] S. W. Benson, "The Foundations of Chemical Kinetics," The McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 256.

[49] A packed reactor was not employed because of technical difficulties resulting from the relatively greater instability of the solid sulfonyl chloride and its low vapor pressure.

In these steps, k_2, k_3, and k_4 must be very large for the radicals not to react with toluene or oxygen added as scavenger. This would be the case if the products from (1) reacted before desorption from the wall took place.

A significant comparison of the rate of decomposition at 65° as the solid and in the vapor phase (calculated) and in hydrocarbon solvents is given in Table V.

TABLE V

VARIATION OF DECOMPOSITION RATES OF TRIMETHYLMETHANESULFONYL CHLORIDE WITH SOLVENT AT 65°

Solvent	10^6k, sec^{-1}
None, solid phase	120
None, vapor phase (calcd)	10
n-Hexane	5.99 ± 0.43
n-Heptane	6.29 ± 0.17
n-Octane	4.25 ± 0.12
n-Tetradecane	3.55 ± 0.02
o,p-Xylene[a]	1.12 ± 0.11

[a] Commerical mixture of isomers.

With present information, there appears to be no way to distinguish in the case of the vapor phase decomposition between an intramolecular and a heterogeneous nonchain process or, in the case of the liquid phase, decomposition between an intramolecular and a radical process in a solvent cage. This can be determined by observing if scrambling occurs on decomposing a mixture containing appropriately labeled (C and Cl) and unlabeled sulfonyl chloride in the first case.

Experimental Section

Kinetic Methods.—When heated in solution, trimethylmethanesulfonyl chloride decomposes to give sulfur dioxide, isobutylene, *t*-butyl chloride, and hydrogen chloride. Sulfur dioxide was the only volatile product from the decomposition of the bridgehead sulfonyl chlorides. As 1 mole of sulfur dioxide is formed for each mole of sulfonyl chloride decomposing, the rate of evolution of dioxide provides a simple means for following the decomposition rate. Rate constants were evaluated using the method devised by Kice[50] whereby evolved sulfur dioxide was swept out by nitrogen into aliquots of standard iodine solution which decolorized when an equivalent amount of sulfur dioxide had passed in. Rate constants were computed by an IBM 1620 computer using a least-squares solution for *k* in the equation $\ln (a - x) = -kt + c$.

Decomposition of trimethylmethanesulfonyl chloride in the vapor phase was studied by observing pressure changes in a low-pressure static system employing a 1-l. glass reactor and also by gas-liquid partition chromatography of samples periodically withdrawn from the system. Pressures were measured using a mercury in glass capillary manometer read with the aid of a cathetometer.

Gas-liquid partition chromatographic analyses were made using a dual column Micro Tek Model GC 2500 modified chromatograph equipped with a thermal conductivity detector. A Model 205 mechanical Disc intergrator was used with a Barber-Colman recorder for measurements of peak areas. It was found that sulfur dioxide, isobutylene, and *t*-butyl chloride could be separated easily using a $^1/_4$ in. × 6 ft column packed with dodecyl phthalate on 60–80 mesh Chromosorb P.

After no further change in pressure for 24 hr it was shown, by absorbing in standard iodine solution and titration of the remaining iodine with thiosulfate, that the decomposition gave 98% of the theoretical amount of sulfur dioxide.

The sulfonyl chloride, being relatively unstable in the solid phase and having a low vapor pressure, underwent some decomposition before it had completely vaporized. Because of this, the lowest practicable operating temperature was about 90°.

The vapor phase rate constants showed very little error and were accurate first-order ones after cessation of solid phase decomposition and after complete sublimation of the sample. Reproduction of rate constants depended critically on purity, only material melting at or above 94.5° giving good results. Rate constants were computed using a least-squares solution for *k* in the equation $\ln (P_\infty - P_T) = \ln (P_\infty - P_0) - kt$.

Preparation of Trimethylmethanesulfonyl Chloride.—Excess sulfur dioxide was bubbled rapidly into a cold (5°) ether solution of *t*-butylmagnesium chloride prepared from 137 g (1.48 mole) of *t*-butyl chloride. The resulting sulfinic acid salt was used in the following ways to prepare the sulfonyl chloride.

From the Sulfinic Acid Salt.—From an addition funnel, 200 g (1.48 moles) of sulfuryl chloride was added slowly over a period of 2 hr to the ethereal sulfinic acid salt solution. The resulting white slurry was hydrolyzed by pouring onto ice, the ether layer was separated and evaporated to near dryness, and the crude solid sulfonyl chloride (about 70 g) was isolated, then dissolved in 200 ml of *n*-pentane, and dried with anhydrous magnesium sulfate. Most of the pentane was evaporated and 60.5 g (0.386 mole) of trimethylmethanesulfonyl chloride was recovered, a yield of 26% based on *t*-butyl chloride. The sulfonyl chloride was stored at −20° and sublimed under vacuum in small portions immediately before use. Sublimation gave material melting at 95–95.5°

Anal. Calcd. for $C_4H_9ClSO_2$: C, 30.9; H, 5.79; Cl, 22.6; S, 20.4. Found: C, 30.9; H, 5.68; Cl, 22.9; S, 20.6.

The nmr spectrum in carbon tetrachloride showed a single peak at δ 1.63, relative to tetramethylsilane, attributable to the nine protons of the *t*-butyl group.

Since the melting point of analytically acceptable sublimate prepared earlier by the Cherbuliez process melted at 89–91°,[17a] it is evident that the molal freezing point depression constant for this material must be quite high.

From the Sulfinic Acid.—The magnesium sulfinate solution from 137 g (1.48 moles) of *t*-butyl chloride was poured into a cold saturated solution of ammonium chloride. After stirring, the ether layer was removed, dried, and evaporated to give 108 g (0.885 mole) of crude sulfinic acid. Sulfuryl chloride was added dropwise with stirring to 38 g of the sulfinic acid until the rapid evolution of gases ceased. The resulting slurry was extracted with pentane, and the extract was washed with water, dried, and evaporated to dryness to yield 41 g (0.262 mole) of sulfonyl chloride, mp 91–92°, a yield of 50% based on *t*-butyl chloride. Vacuum sublimation gave material melting at 95–95.5°. The infrared spectrum was identical with that from the sulfonyl chloride prepared from the sulfinic acid salt.

Preparation of N-Cyclohexyltrimethylmethanesulfonamide.—At a rate just sufficient to maintain a gentle reflux, 8 g (0.114 mole) of chlorine was bubbled into a solution of 20 g (0.112 mole) of *t*-butyl disulfide [bp 195–196° (755 mm), n^{25}D 1.4828–1.4855] in 300 ml of isopentane. The mixture was added slowly to 60 g (0.41 mole) of cyclohexylamine (n^{25}D 1.4553) and the solvent was evaporated after the reaction mass had been washed with water. There was obtained 26 g (0.14 mole) of the crude sulfenamide. Saturated potassium permanganate solution was added slowly to 10 g of it in 150 ml of acetone until the permanganate color persisted. The solution then was filtered and cooled, depositing 5.5 g of N-cyclohexyltrimethylmethanesulfonamide as white needles, mp 117–118°, a yield of 47% based on the disulfide. Two recrystallizations from isooctane left the melting point unchanged.

Anal. Calcd for $C_{10}H_{22}NO_2S$: C, 54.75; H, 9.95; N, 6.39; O, 14.59; S, 14.62. Found: C, 54.96; H, 9.80; N, 6.18; O, 14.70; S, 14.77.

The infrared spectrum shows the characteristic SO_2 bands at 1310 and 1130 cm^{-1} and the free N-H band at 3386 cm^{-1}. In addition, there is a bonded N-H absorption at 3268 cm^{-1}, the intensity of which shows strong solvent concentration effects as does the asymmetrical SO_2 band at 1310 cm^{-1}. This apparent dimerization might be related to the peculiar property of this substance being largely insoluble in aqueous alkali.

Preparation of Bridgehead Sulfonyl Chlorides.—The hydrocarbons *sym*-bicyclooctane[13] and adamantane[9] were chlorosulfonylated in carbon tetrachloride solution (10 and 16 g/100 ml, respectively) at 10–15° using a mixture of sulfur dioxide and chlorine (1.3 to 1.0 mole ratio) and irradiated by a 150-w G. E. Par 38 projector flood lamp until sufficient chlorine had been admitted for 50–65% of the hydrocarbon to have been converted to the monosulfonyl chlorides. The solvent was removed under vacuum; the residue was extracted with liquid sulfur dioxide which

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(50) J. L. Kice, F. Parham, and R. Simons, *J. Am. Chem. Soc.*, **82**, 834 (1960).

had been treated with decolorizing charcoal.[51] The extracts were cross-extracted with hexane to remove any residual hydrocarbons or chlorinated hydrocarbons from the sulfonyl chlorides and the sulfur dioxide was allowed to boil off. The monosulfonyl chlorides were extracted from the polysulfonyl chlorides with pentane, at $-25°$ in the case of the bicyclooctane products, at room temperature in the case of the adamantane. The pentane was distilled off to leave viscous oils. No physical properties were determined in the case of the bicyclooctane product; in the case of adamantane they were $n^{20}\mathrm{D}$ 1.5412, d^{20}_4 1.3070, $M\mathrm{D}$ 55.78 (calcd 55.46).

Since attempts to separate the mixture of isomeric monosulfonyl chlorides were unsuccessful, these mixtures were used in the kinetic studies.

Derivatization of the Sulfonyl Chlorides.—The residue from thermal decomposition of the *sym*-bicyclooctanesulfonyl chlorides was treated with liquid ammonia to yield the same sulfonamide from the known secondary sulfonyl fluoride, mp 132–133°.[15]

The mixture of adamantanesulfonyl chlorides, in chloroform and freed of polysulfonyl chlorides, was treated with liquid ammonia to give a sulfonamide, mp 208.5–209.5°, believed to be the secondary isomer.

Anal. Calcd. for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51; S, 14.89. Found: C, 55.64; H, 7.88; N, 6.54; S, 14.92.

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[51] This treatment evidently removes some impurities in commercial grade sulfur dioxide and results in lighter colored, more stable sulfonyl chlorides.[9]

Group Electronegativity and Polar Substituent Constants

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The relationship between polar substituent constants (σ^*) and group electronegativity values calculated by the method of electronegativity equalization has been examined. It is found that the best correlation is between σ^* and the charge (δ) induced on the carbethoxy group as calculated from group electronegativity. If one assumes partial (instead of complete) equalization of electronegativity, the correlation is improved. Using 80% equalization, the relation ($\sigma^* = -12.84\delta + 3.54$; $r = 0.97$) is obtained for 47 organic groups. The use of partial equalization also obviates the difficulties in isomeric group electronegativities previously encountered.

The recently developed concepts of orbital electronegativity[1-3] and electronegativity equalization[2,4-6] have permitted facile calculation of electronegativities for σ-[2,7] and π-bonded[8] groups. However, two problems have confronted the use of group electronegativities: (1) the relatively simple procedures previously suggested yield, contrary to chemical intuition, identical values for all isomers of a group (assuming identical valence states); (2) the more inclusive and important question may be asked concerning the general validity and usefulness of the method. Group electronegativities calculated by Jaffé and co-workers[2] have been shown to correlate with various physical and chemical properties[9] and these same methods have proven useful in discussing charge distribution and nmr coupling constants.[10] However, no widespread comparison of the many available group values with experimental data has yet been made. The principal reason for this is that most of the empirically derived group electronegativities are restricted to a limited number of groups, often determined and applicable only under special circumstances. It is the purpose of the present investigation to examine the relation between calculated group values and empirical data and thereby establish confidence limits in using the former. In addition, it was found that methods developed in the present study obviate objections based on isomeric group electronegativities.

Polar Substituent Constants.—Although electronegativity has proven to be very useful to the inorganic chemist in explaining various phenomena,[11] it has been of limited usefulness to the organic chemist. Some attempts have been made to set up electronegativity scales for organic groups, but they have not been particularly successful. In contrast, data for a large number or reactions have been interpreted successfully in terms of the *polar substituent constant*, σ^*, and related parameters.[12] These parameters should reflect the charge distribution in a molecule (or more accurately, in an activated complex) under consideration and thus be related to the electronegativity of the substituent groups. Jaffé[2] plotted the electronegativities of halomethyl groups *vs.* their σ^* values and found reasonably good agreement if chlorine, bromine, and iodine were assumed to be hybridized to contain some *s* character.

In the present work it was found that, if the electronegativity, a, of a group is plotted *vs.* its polar substituent constant, there is a tendency for a linear relationship to hold, but the fit is not very close ($r = 0.84$). One should expect that since σ^* is a reaction parameter, it should be a function of the charge induced at the reaction site rather than of the inherent electronegativity *per se*. The charge distribution in molecules is a function of both the inherent electronegativity, a, and the charge coefficient, b.[7] However, when the partial charge, δ, is plotted *vs.* σ^*, it is found that the preciseness of fit worsens ($r = 0.30$). This rather surprising result indicates that, in general, the values of b are somewhat less accurate than the values of a. Inspection of those groups which seem to deviate most from a linear relationship with σ^* indicates that they are the higher alkyl groups with calculated low values of b (predicted to be better donators than they really are) or Ω-substituted-nitro- and -fluoroalkyl

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