chloride. After 30 min, the solvent was removed and a solid remained, mp 86–87°. The nmr was consistent with α-(*N*-phenyl-*N*-methylcarbamoyl)-α-chloromethyl benzyl sulfide: a multiplet at τ 2.9 (aromatic), a heptet at τ 5.2 ($CHMe_2$), a singlet at τ 5.2 (CHCl), a singlet at τ 6.1 (CH_2), and a doublet at τ 9.0 [$CH(CH_3)_2$]. The yield was 86%.

Anal. Calcd for $C_{18}H_{20}ClNOS$: C, 64.75; H, 6.04; N, 4.20. Found: C, 64.86; H, 5.91; N, 4.21.

In order to ensure that the chlorine was assigned to the correct position, it was hydrolyzed by acidic 2,4-DNP reagent. A solid formed which was recrystallized from ethanol, mp 192–192.5°. Its elemental analysis was consistent with the DNP derivative of *N*-phenyl-*N*-isopropyl glyoxyamide.

Anal. Calcd for $C_{17}H_{17}N_5O_5$: C, 54.98; H, 4.61; N, 18.86. Found: C, 54.73; H, 4.68; N, 18.64.

The reaction was repeated with 2 equiv of deuteriomethanol added before the addition of sulfuryl chloride. The nmr of the product was identical with that shown above. The mass spectrum of the product indicated less than 5% deuterium incorporation in the highest mass found, *m/e* 265. This fragment is apparently a result of a Ramberg–Bachlund type rearrangement.

Chlorination of a Mixture of α-(*N*-Phenyl-*N*-isopropylcarbamoyl)-α,α-dichloromethylsulfenyl Chloride and *p*-Chlorophenacyl-α,α-dichloromethylsulfenyl Chloride.—To a mixture of 7.5 g (0.025 mol) of **2a** and 5.0 g (0.025 mol) of **3b** in *ca.* 100 ml of ethylene dichloride was dropped in 10 g (0.075 mol) of sulfuryl chloride. At the end of the addition, the nmr of the reaction mixture showed a SCH_3 (τ 7.5) and no methyl chloride. At the end of 2 days the SCH_3 peak was nearly gone but a SCH_2Cl peak (τ 5.0) had appeared. The integration showed nearly a quantitative conversion to **5b**.

Registry No.—**2a**, 31328-46-8; **2c**, 31328-47-9; **2d**, 31328-48-0; **2e**, 31328-49-1; **2f**, 31328-50-4; **2g**, 31428-86-1; **2h**, 31328-51-5; **2i**, 31328-52-6; **4b**, 31428-87-2; **5a**, 31328-53-7; **8**, 31385-53-2; **16**, 31328-54-8; **17**, 31385-54-3; **19**, 31328-55-9; α-benzylthiomethyl phenyl sulfone, 31328-56-0; α,α-dichloro-α-phenylsulfonylmethyl benzyl sulfide, 31328-57-1; α-(*N*-phenyl-*N*-methylcarbamoyl)-α-chloromethyl benzyl sulfide, 31328-58-2; *N*-phenyl-*N*-isopropyl glyoxyamide 2,4-DNP, 31328-59-3.

An Ultraviolet Spectroscopy Study on Sulfonium Salts and on an Interaction between Sulfonium Salts and Molecular Oxygen

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The ultraviolet absorption spectra of various trialkyl-, alkyldiaryl-, and triarylsulfonium salts were measured in a nitrogen atmosphere and in an oxygen atmosphere at -40 ± 1 to $25 \pm 1°$. A high intensity band near 200 $m\mu$ was found in these spectra and assigned to be a transition of nonbonding $3p_z$ lone-pair electon of the central sulfur to a vacant 3d sulfur orbital $[(3p_z)^2 \rightarrow (3p_z)(3d)]$. The calculation by the use of ASMO–SCF method well explained this transition band. Solvents used for these measurements exhibited a noticeable effect on the excitation energy of the transition. In a nitrogen atmosphere, nonpolar solvents allowed the transition at longer wavelengths than polar ones. This solvent effect may closely relate to the nature of 3d sulfur orbitals caused by the interaction with the solvents. In an oxygen atmosphere, this band shifted to longer wavelengths in the order of 0.05–0.25 eV. This red shift caused by oxygen increased with the decrease in the dielectric constants of the solvents. Finally, the interaction between the sulfonium salt and molecular oxygen was briefly discussed in connection with the red shift caused by oxygen.

Many chemical studies on the ultraviolet absorption spectra of various sulfur compounds have been made[2–6] with particular reference to the d–π conjugation. Notwithstanding these studies of the ultraviolet spectra, particularly of sulfides,[2–8] sulfones,[2,4,9–12] sulfoxides,[4,12–15] and sulfonium salts,[14–18] the absorption band attributed to the excitation of sulfur atom has not been clarified satisfactorily as yet because of a lack of sufficient knowledge about the bond nature of these sulfur compounds and the shell expansion of their d orbitals. In connection with our previous studies[19–22] on the catalytic properties of sulfonium compounds in the liquid phase hydrocarbon oxidation, it was required necessarily to study the ultraviolet spectra of sulfonium salts and those in the presence of molecular oxygen.

Concerning the latter, ultraviolet spectroscopic studies of the interaction between organic compounds and molecular oxygen have been recently developed by Evans,[23] Munck and Scott,[24] and Tsubomura, *et al.*[25,26] These studies have been based on the charge-transfer theory of Mulliken,[27–30] namely, on "contact

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charge-transfer" spectra which are, hence, attributed to the interaction between electron donor groups (organic compounds) and electron acceptor ones (oxygen molecule), and it has been found that this interaction relates directly to the ionization potential of solvents. However, on the interpretation of this kind of interaction, some obscurities still remain. It is found in the present paper, however, that the interaction between sulfonium salt and molecular oxygen is much weaker than the usual charge-transfer interaction mentioned above. Therefore, the interaction needs to be investigated from another point of view as will be developed in the present paper.

In the present paper, the absorption spectra of some onium salts, in particular of sulfonium ones, were investigated and, subsequently, the shifts spectra in the presence of oxygen molecules were studied in order to clarify the interaction between the sulfonium salt (as an oxidation catalyst) and oxygen molecule. The experiments were carried out in a nitrogen atmosphere and in an oxygen atmosphere in the temperature range from -40 ± 1 to 25 ± 1°. The excitation energy of singlet or triplet transition of sulfonium salt was then calculated by a zero-differential overlap approximated ASMO-SCF method to discuss the transition energy of the electrons in the sulfur atom. Finally, the interaction between sulfonium salts and molecular oxygen was briefly discussed.

Experimental Section

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were measured with a Beckman quartz spectrometer with a hydrogen discharge tube source, using 1-cm cells with a ground glass stopper. Ethyl alcohol, water, and isopropyl alcohol solutions of various sulfonium salts were prepared under a nitrogen atmosphere and the concentration of the solution was kept about 10^{-5} mol/l. The solvents used for the measurements were specially prepared reagents for spectroscopy and were subjected to the preparation of the solution without further purification. The measurements were made at 0 and −40° by flowing the cold methyl alcohol (made by Dry Ice-methyl alcohol solution) and also at 25 ± 1°. At first, the sample and reference solutions filled with dry nitrogen (by bubbling for at least 1.5 min) were subjected to the measurements and next were run in the same way with dry oxygen. After that, dry nitrogen was bubbled again into both solutions and the absorption spectrum was measured once more. During the measurement, a dry nitrogen atmosphere was required around the spectrometer under a slightly positive pressure in order to avoid the influence of oxygen. For all measurements, the absorption spectra of the solution filled with dry nitrogen recorded at the first time were in good agreement with those recorded at the second time.

Preparation of Onium Salts. Trialkylsulfonium Tetrafluoroborates.—Trimethylsulfonium and tri-*n*-butylsulfonium tetrafluoroborate were prepared by the same method as in a previous paper.[31] Analytical data are given as follows: $(CH_3)_3SBF_4$, mp 307–308° dec (Found: BF_4, 52.3. Calcd for $C_3H_9SBF_4$: BF_4, 52.9); $(n\text{-}C_4H_9)_3SBF_4$, mp 92–95° (Found: BF_4, 33.2. Calcd for $C_{12}H_{27}SBF_4$: BF_4, 32.8).

Dimethyl *n*-Butylsulfonium Tetrafluoroborate.—An aqueous solution of silver tetrafluoroborate (20 ml, 0.05 mol) was added to ethyl alcohol solution (200 ml) of methyl di-*n*-butylsulfonium iodide synthesized from di-*n*-butyl sulfide and methyl iodide and the solution was stirred vigorously for *ca.* 1 hr. The precipitates of silver iodide were filtered off and the filtrates evacuated in a nitrogen atmosphere to obtain the crystals of $(CH_3)_2(n\text{-}C_4H_9)SBF_4$ melting at 67.5–68.0° (Found: BF_4, 42.3. Calcd for $C_6H_{15}SBF_4$: 42.2).

Trimethylsulfonium Bromide and Iodide.—An aqueous solution of potassium bromide or iodide (10 ml, 0.4 mmol) was added to a water (20 ml)–ethyl alcohol (30 ml) solution of trimethylsulfonium tetrafluoroborate (0.35 mmol) and quenched and distilled at a temperature below 40° *in vacuo* to obtain a syrup, which was treated by absolute ethyl alcohol–petroleum ether (bp 30–60°) to afford rough crystals. These rough crystals were recrystallized from methyl alcohol and ether and dried by phosphorus pentoxide to give $(CH_3)_3SBr$ or $(CH_3)_3SI$ melting at 177–178 dec or 214–215° dec, respectively (Found: Br, 50.3. Calcd for C_3H_9SBr: Br, 50.9. Found: I, 62.0. Calcd for C_3H_9SI: I, 62.2).

Triphenylsulfonium-, Triphenylselenonium-, and Triphenyltelluronium Chloride.—An aqueous solution of potassium phosphate (20 ml, 0.4 mmol) was added to ethyl alcohol (200 ml) solutions of triphenylsulfonium, triphenylselenonium, and triphenyltelluronium tetrafluoroborates (1 mmol) prepared by the methods similar to those reported in a previous paper,[32] and the solutions were kept standing for about 24 hr. The precipitates of potassium tetrafluoroborate were filtered off and the filtrates evacuated in a nitrogen atmosphere. The raw crystals were recrystallized from chloroform and ether to afford the following (white needles): $(C_6H_5)_3SCl$, mp 297–298° (Found: Cl, 11.6. Calcd for $C_{18}H_{15}SCl$: Cl, 11.9); $(C_6H_5)_3SeCl$, mp 229–230° (Found: C, 56.6; H, 4.5. Calcd for $C_{18}H_{15}SeCl$; C, 57.2; H, 4.5); and $(C_6H_5)_3TeCl$, mp 225° dec (Found: C, 17.3; H, 4.5. Calcd for $C_{18}H_{15}TeCl$: C, 17.3; H, 4.4).

Triphenylsulfonium Phosphate.—An aqueous solution of potassium phosphate (20 ml, 0.4 mmol) was added to an ethyl alcohol solution (200 ml) of triphenylsulfonium tetrafluoroborate (1 mmol). The solution was treated similar to the case of $(C_6H_5)_3SCl$ to obtain colorless needles of $(C_6H_5)_3S\cdot{}^1/_3PO_4$ melting at 201–201.5° (Found: C, 72.2; H, 5.09. Calcd for $C_{54}H_{45}S_3PO_4$: C, 72.0; H, 5.11).

Alkyldiphenylsulfonium Tetrafluoroborate.—Equimolar amounts of diphenyl sulfide and silver tetrafluoroborate were kept standing at room temperature to precipitate dark brown crystals which were dried *in vacuo*. Hygroscopic dark brown crystals of the diphenyl sulfide–silver fluoroborate complex (90% yield) were obtained which melted at 54–55° dec. (Found: C, 38.5; H, 2.5. Calcd for $C_{12}H_{10}SBF_4Ag$: C, 37.9; H, 2.6). Alkyl iodide (0.08 mol) was added to an ethylene chloride solution of the complex (0.056 mol). The solution was stirred for *ca.* 2 hr at room temperature and left standing overnight to precipitate silver iodide which was removed. After the solvent was removed from the nitrogen atmosphere, crystals were obtained and recrystallized from chloroform and ether. Analytical data of the products are as follows: $CH_3(C_6H_5)_2SBF_4$, mp 61–62° (Found: BF_4, 30.5. Calcd for $C_{13}H_{13}SBF_4$: BF_4, 30.9); and $n\text{-}C_4H_9(C_6H_5)_2SBF_4$, mp 85–86° (Found: BF_4, 26.3. Calcd for $C_{16}H_{19}SBF_4$: BF_4, 27.1).

Alkyldiphenylsulfonium Perchlorate.—Diphenyl sulfide (5 g) and 5.8 g of silver perchlorate were stirred vigorously until a reddish color disappeared to precipitate dark brown crystals. Hygroscopic dark brown crystals of diphenyl sulfide–silver perchlorate complex (10.8 g) were obtained which melted at 62–63° dec (Found: C, 37.5; H, 2.9. Calcd for $C_{12}H_{10}O_4SClAg$: C, 36.7; H, 2.6). The mixture of the phenyl sulfide–silver perchlorate complex (0.027 mol) and *n*-butyl iodide (0.04 mol) was treated similarly as mentioned above to obtain white needles of *n*-butyldiphenylsulfonium perchlorate (65% yield) melting at 107–108° (Found: ClO_4, 29.1. Calcd for $C_{16}H_{19}SClO_4$: ClO_4, 29.0).

Method of Calculation.—In order to determine the molecular structures of sulfonium salts, trimethylsulfonium chloride was selected as a sulfonium salt for the convenience of calculations using the zero-differential overlap approximated ASMO-SCF method. For the calculations, the bond distances and angles of trimethylsulfonium chloride were set up as follows: S–C = 1.82, S–Cl = 2.5–4.5, C–H = 1.10 Å; ∠HCH = 109° 28 min, ∠CSCl = 90–109° 28 min.

The values of orbital exponents calculated by Clementi and Raimondi[33] were used for s and p orbitals, and the ionization po-

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TABLE I

ULTRAVIOLET SPECTRA OF ALKYLSULFONIUM SALTS IN A NITROGEN ATMOSPHERE

Compd	Solvent[a]	Temp, °C	¹W, λ max (log ε)	λ max (log ε)
Me_3SBr	E	25 ± 1	232 (2.87)	201.5 (3.58)
Me_3SI	H	25 ± 1	227.5 (4.50)	195 (4.50)
n-$BuSMe_2BF_4$	E	25 ± 1	228 (3.10)	203 (3.67)
$(n\text{-}Bu)_3SBF_4$	E	25 ± 1	228.5 (3.81)	197.5 (4.10)
Me_3SBr	E	5 ± 1	231 (2.79)	200.5 (3.46)
Me_3SBr	E	0 ± 1	230 (2.82)	200 (3.54)
Me_3SI	H	0 ± 1	227 (4.47)	193 (4.77)

[a] E, absolute ethanol; H, water.

TABLE II

ULTRAVIOLET SPECTRA OF TRIPHENYLSULFONIUM SALTS (N_2–N_2 SYSTEM)[a]

			¹Lb		¹La,	
Compd	Solvent	Temp, °C	λ max (log ε)	λ max (log ε)	λ max (log ε)	λ max (log ε)
Ph_3SCl	E	25 ± 1	276 (3.40)	269 (3.59)	227 (4.65)	204 (4.76)
Ph_3SCl	H	25 ± 1	276 (3.33)	268 (3.56)	232 (4.25)	194 (4.85)
Ph_3SBF_3	E	25 ± 1	276 (3.40)	268.5 (3.59)	232 (4.28)	204 (4.76)
$Ph_3S.{}^1/_3PO_4$	E	4 ± 1	277.5 (3.74)	270 (3.80)	235 (4.00)	204 (4.68)
Ph_3SBF_4	E	4 ± 1	277 (3.88)	269.5 (3.55)	232.5 (4.68)	205 (5.15)
Ph_3SCl	H	0 ± 1	277 (3.56)	269 (3.56)	232.5 (4.29)	197.5 (4.85)
Ph_3SCl	E	−40 ± 1	276 (3.58)	270 (3.66)	232 (4.27)	202.5 (4.71)
Ph_3SBF_4	E	−40 ± 1	276 (4.03)	268 (3.71)	233 (4.30)	201 (4.62)
Ph_4PCl[b]	E	25 ± 1	276 (3.57)	269 (3.65)[c]		204 (4.81)

[a] Sample and reference cells were in the nitrogen atmosphere. [b] Adsorption bands of this compound were recorded for comparison. [c] An additional peak was found at 262 mμ (3.48).

tentials and electron affinities[34] were cited from the reference of Hinze and Jaffé.[35a] For the sulfur 3d orbital, the orbital exponent was taken to be 1.0, and the ionization potential and electron affinity were adopted from the data of Levison and Perkins.[35b]

Results

(1) Absorption Spectra of Trialkylsulfonium Salts.—The ultraviolet spectra of trialkylsulfonium salts in ethyl alcohol (or in water) filled with dry nitrogen at the temperature range from −40 ± 1 to 25 ± 1° indicated a high intensity absorption band near 200 mμ as is shown in Figure 1 and Table I. In this case, the dry nitrogen plays an important role to avoid the appearance of charge-transfer peaks[12] near 200 mμ caused by an interaction between solvents and the oxygen molecule which may dissolve as a contaminant. The counteranion does not influence directly the peak near 200 mμ, which denies that this peak would correspond to the intramolecular charge-transfer transition between the sulfonium ctaion and the anion.

(2) Absorption Spectra of Triarylsulfonium Salts.—In the case of diphenyl sulfide, Mauthner[36] reported the two maximum peaks at 277 mμ (log ε 3.76) and 250 (4.08) as ¹L$_b$ transition in ethanolic solution. It is worthy of emphasis here that diphenyl sulfide was found to indicate further peaks of 231 mμ (log ε 3.87) as ¹L$_a$ transition and an additional one at 206 mμ (log ε 4.50) in a nitrogen atmosphere (Table II). The absorption spectra of triphenylsulfonium salts in ethyl alcohol (or in water) filled with dry nitrogen were measured at the temperature range from −40 ± 1 to 25 ± 1°. The absorption bands are listed in Table II. Phenyl substituents of the central sulfur of the sulfonium cation have also ¹L$_a$ transition at near 232 mμ (log ε ~4.3). An additional high intensity peak at *ca.* 200 mμ (log ε ~4.7) is also recognized in the spectra of sulfonium salts.

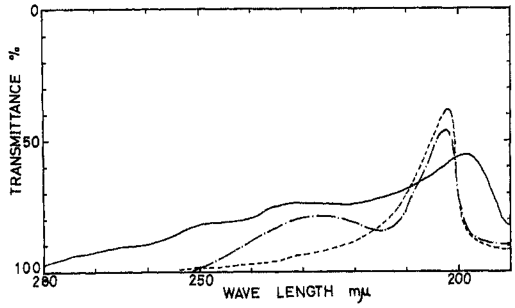

Figure 1.—Absorption spectra of trialkylsulfonium salts in C_2H_5OH under nitrogen atmosphere: ——, $(C_4H_9)_3SBF_4$ (2.02×10^{-5} mol/l.) at −40 ± 1°; —·—; $(n\text{-}C_4H_9)(CH_3)_2SBF_4$ (7.29×10^{-5} mol/l.) at 25 ± 1°; ------, $(CH_3)_3SBr$ (9.56×10^{-5} mol/l.) at 25 ± 1°.

(3) Spectra of Alkyldiarylsulfonium Salts.—The absorption spectra bands of alkyldiphenylsulfonium salts in ethyl alcohol are recorded in Table III, from which a strong absorption band near 200 mμ was also recognized.

Ultraviolet Spectra of Sulfonium Salts in an Oxygen Atmosphere.—Charge-transfer interaction between organic molecules, as electron donors, and the oxygen molecule, as an electron acceptor, has been investigated experimentally by Evans[23] and others,[24–26,37–40] and theoretically by many authors.[25,41,42] We have also tried to investigate the interaction between molecular

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[34] S: Ip (3s) = 20.08, Ea (3s) = 11.54; Ip (3p) = 13.32, Ea (3p) = 3.50; Ip (3d) = 3.06, Ea (3d) = 1.63. C: Ip (2s) = 21.01, Ea (2s) = 8.91; Ip (2p) = 11.27, Ea (2p) = 0.34. H: Ip (1s) = 13.60, Eu (1s) = 0.75. Cl: Ip (3s) = 24.02, Ea (3s) = 14.45; Ip (3p) = 15.03, Ea (3p) = 3.73.

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TABLE III

ULTRAVIOLET SPECTRA OF ALKYLDIPHENYLSULFONIUM SALTS (N_2–N_2 SYSTEM)[a]

			^1L_b			^1L_a,	
Sulfonium salt	Solvent	Temp, °C	λ max (log ε)	λ max (log ε)	λ max (log ε)	λ max (log ε)	λ max (log ε)
$MeSPh_2BF_4$	E	25 ± 1	274 (3.11)	267 (3.24)	261 (3.18)	232 (3.98)	202.5 (4.45)
$MeSPh_2ClO_4$	E	25 ± 1	275 (3.25)	267.5 (3.31)	261 (3.18)	235.5 (3.97)	203.5 (4.42)
$EtSPh_2BF_4$	E	25 ± 1					
$PrSPh_2BF_4$	E	25 ± 1					
n-$BuSPh_2BF_4$	E	25 ± 1	274.5 (3.25)	267.5 (3.36)	261 (3.26)	234 (4.16)	204 (4.51)
n-$BuSPh_2ClO_4$	E	25 ± 1	274.5 (3.26)	267.5 (3.36)	262 (3.26)	236 (4.09)	204 (4.36)
$PhSPh_2BF_4$	E	25 ± 1	276 (3.40)	268.5 (3.59)		232 (4.28)	204 (4.76)
$MeSPh_2BF_4$	E	0 ± 1	274 (3.11)	267 (3.24)	261 (3.18)	232.5 (3.99)	201 (4.42)
$MeSPh_2BF_4$	E	−40 ± 1	273 (3.11)	267 (3.24)	261 (3.18)	232.5 (3.97)	200
$PhSMe_2ClO_4$[b]	H	25 ± 1		265 (3.04)		220 (3.94)	
p-$HOPhSMe_2Cl$[c]	H	25 ± 1		264 (3.66)		242 (4.03)	

[a] Sample and reference cells were in the nitrogen atmosphere. [b] Data cited in the literature: F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, **78,** 87 (1956). [c] Data cited in the literature: S. Oae and C. C. Price, *ibid.*, **80,** 3425 (1958). The authors pointed out an additional peak at 248 mμ (3.62) in the spectrum of *p*-$HOPhSMe_2Cl$.

TABLE IV

ULTRAVIOLET SPECTRA OF SULFONIUM SALTS IN O_2–O_2 SYSTEM[a,b]

Sulfonium salt			^1L_b			^1L_a	$S[(3p_z)^2 \rightarrow (3p_z)(3d)]$	Δλ	
(concn, mol/l. × 10^5)	Temp, °C	λ max (log ε)	λ max (log ε)	λ max (log ε)	λ max (log ε)	λ max (log ε)	mμ[c]	eV
Ph_3SCl (1.67)	25 ± 1	276 (3.40)	269 (3.59)		227 (4.65)	209 (4.73)	+5.0	0.14
Ph_3SCl (6.70)	−40 ± 1	276 (3.58)	270 (3.66)		232 (4.27)	214 (4.23)	+11.5	0.30
Ph_3SBF_4 (1.43)	4 ± 1	277 (3.88)	269.5 (4.03)		232.5 (4.68)	212 (4.59)	+7.0	0.08
Ph_3SBF_4 (1.43)	−40 ± 1	276 (3.58)	268 (3.71)		233 (4.27)	208 (4.32)	+7.0	0.20
$Ph_3S\cdot{}^1/_3PO_4$ (1.70)	4 ± 1	277.5 (3.20)	270 (3.37)		235 (4.03)	210 (4.30)	+6.0	0.17
$MeSPh_2ClO_4$ (2.00)	25 ± 1	275 (3.31)	267.5 (3.40)	261 (3.18)	235.5 (3.89)	206 (3.94)	+2.5	0.05
n-$BuSPh_2ClO_4$ (1.46)	25 ± 1	274.5 (3.26)	267.5 (3.36)	262 (3.26)	234 (4.12)	206.5 (4.35)	+2.5	0.07
$MeSPh_2BF_4$ (2.08)	25 ± 1	274 (3.11)	267 (3.24)	261 (3.18)	232 (3.98)	205.5 (4.42)	+3.0	0.06
$MeSPh_2BF_4$ (2.08)	0 ± 1	274 (3.11)	267 (3.24)	260 (3.24)	232.5 (3.99)	206 (4.32)	+5.0	0.12
Me_3SBr (4.78)	25 ± 1				232 (2.78)	205 (3.50)	+3.5	0.10
Me_3SBr (4.78)	0 ± 1				230 (2.82)	207.5 (3.44)	+7.5	0.25
Ph_4PBr[d] (1.91)	25 ± 1	276 (3.57)	269 (3.65)	262 (3.48)		209 (4.65)	+5.0	0.15

[a] Sample and reference cells were filled with oxygen. [b] Solvent, ethyl alcohol. [c] This value was the difference between the λ max of the assignment [S(3p-lone pair → 3d)] in the O_2–O_2 system and that in the N_2–N_2 system. Positive signs imply the red shift of the former from the latter. [d] Absorption peaks of this compound were listed for comparison.

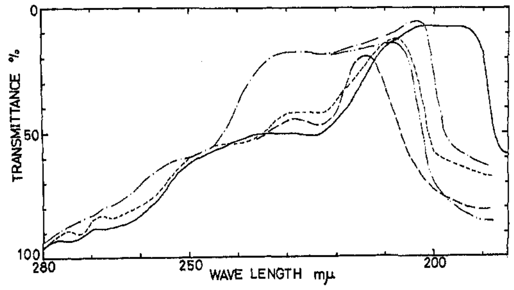

Figure 2.—Absorption spectra of $(C_6H_5)_3SCl$ (1.67 × 10^{-5} mol/l.) at 25 ± 1°: ——, in water (in a nitrogen and an oxygen atmosphere); — · —, in ethanol (in N_2); — · · —, in ethanol (in O_2); - - - - - -, in 2-propanol (in N_2); — — —, in 2-propanol (in O_2).

oxygen and sulfonium salts which are known to be particularly effective as an oxidation catalyst for hydrocarbon oxidations.[19–20] The absorption band and the intensity of the sulfonium salt in the presence of molecular oxygen are listed in Table IV. The absorption band near 200 mμ indicated the red shift in the order of 0.05–0.25 eV and a somewhat lower intensity in comparison with that in a nitrogen atmosphere. It is assured from the shift of the absorption band caused by oxygen that the interactions are appreciably weaker than the ordinary charge–transfer transitions between organic compounds and molecular oxygen. Furthermore, from Table IV, the lower temperature promotes the red shift to the longer wavelength remarkably. This may be attributed to an enhancement[21] of the interaction of the sulfonium with molecular oxygen. Moreover, this red shift is affected notably by the solvent used for the measurement of spectra.

Solvent Effect on the Absorption Spectra of Triphenylsulfonium Chloride.—In the case of such a salt as the sulfonium one, the transition wavelength is affected considerably by the polarity of the solvent because the polar solvent stabilizes remarkably the sulfonium ion through the orientation of the solvent. The absorption spectra of triphenylsulfonium chloride measured in water, ethyl alcohol, and isopropyl alcohol are shown in Figure 2.

Absorption Spectra of Triphenylsulfonium, -selenonium, and -telluronium Chlorides.—The spectra of onium salts which have different central atoms are shown in Figure 3, where the absorption bands near 200 mμ are also recognized. In an oxygen atmosphere, the absorption bands of the transition were shifted to the longer wavelength than those in a nitrogen atmosphere, being in the order of 0.15, 0.105, and 0.09 eV for sulfonium, selenonium, and telluronium chloride, respectively.

Determination of the Molecular Structure of Sulfonium Salts.—Before speaking about the transition band of sulfonium salts, it is necessary to determine the structures of the salts in order to assign the bands. ASMO–SCF calculations were performed on trimethyl-

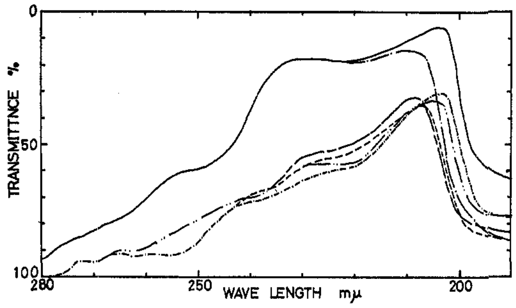

Figure 3.—Absorption spectra of onium chlorides in C_2H_5OH at 25 ± 1°: 1.67×10^{-4} mol/l., $(C_6H_5)_3SCl$ in a nitrogen atmosphere (——), in an oxygen atmosphere (— · —); 1.45×10^{-5} mol/l., $(C_6H_5)_3SeCl$ in a nitrogen atmosphere (- - - - -), in an oxygen atmosphere (— — —); 1.40×10^{-5} mol/l., $(C_6H_5)_3$ TeCl in a nitrogen atmosphere (— · · —), in an oxygen atmosphere (— · —).

sulfonium chloride changing the bond angle of ∠CSCl from 90° to 109° 28 min at a fixed distance of S–Cl (3.5 Å) considering that the counteranion of the salt may be apart at or beyond a van der Waals distance (*ca.* 3.5 Å) from the central sulfur atom in such polar solvents as ethyl alcohol. The calculated results of atom populations, total energies (E_{HF}), and dipole moments (μ) are shown in Figure 4. From the minimum value of E_{HF} at ∠CSCl 90° indicated in Figure 4, an appropriate molecular structure of the sulfonium cation takes a sp^2 hybrid conformation as already reported.[22] Furthermore, the calculations were performed also on trimethylsulfonium chloride changing the bond distance of S–Cl from 2.5 to 4.5 Å at fixed angles of ∠CSCl and ∠CSC (90 and 120°, respectively). The values of calculated E_{HF} indicated in Figure 5 emphasize that the most stable conformation of the salt is found at S–Cl = 4.5 Å. The bond distance of S–Cl may be 3.5–4.5 Å in the reaction condition.

Discussion

In the first place, it is necessary to clarify the transition in sulfur compounds such as sulfonium salts. Fehnel and Carmack[3] demonstrated that a series of alkyl sulfides such as methyl and ethyl sulfide, etc., had strong intensity bands near 210 mμ (log $\epsilon \sim 3$). Leandri and his coworkers[12] reported also the strong absorption band of the sulfoxides near 220 mμ. In the case of alkyl sulfones,[3] this peak near 210 mμ appears below 210 mμ. From these investigations, it is conjectured that the transition band in the neighborhood of 200 mμ is assigned to be the excitation of electrons on sulfur orbitals. Through the absorption spectra of trialkyl-, triphenyl- and alkyldiphenylsulfonium salts in nitrogen atmosphere, the absorption band near 200 mμ may be related to the transition of the 3p lone-pair electron to an unoccupied 3d sulfur orbital.

Excitation Energy of the Sulfonium Salt.—In order to assure the assignment of the band, the transition energies to trimethylsulfonium chloride were calculated by the ASMO-SCF method. Singlet excitation energies and the energy levels of the orbitals of trimethylsulfonium chloride are indicated in Figure 6. From Figure 6, it is found that the transition of the $(3p_z)^2$ lone-pair electrons to the low-lying unoccupied 3d orbitals (5.22–6.65 eV) well explains the absorption range of 215 mμ (5.77 eV)–195 mμ (6.36 eV). In connection with the excitation energies of trimethylsulfonium chloride, it is necessary here to discuss the absorption bands of sulfonium salts in alcoholic solutions.

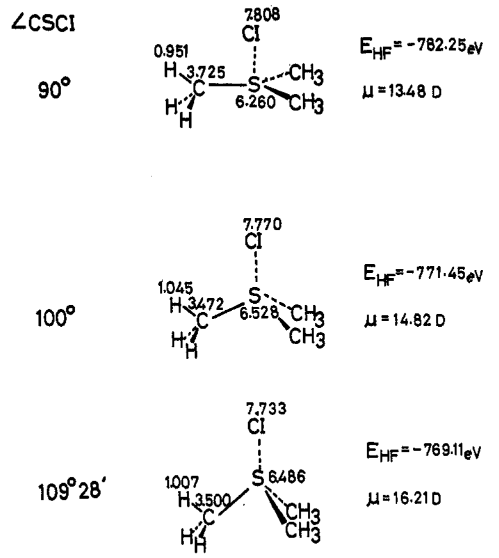

Figure 4.—The variation of the electronic state of $(CH_3)_3SCl$ with the bond angle of <CSCl.

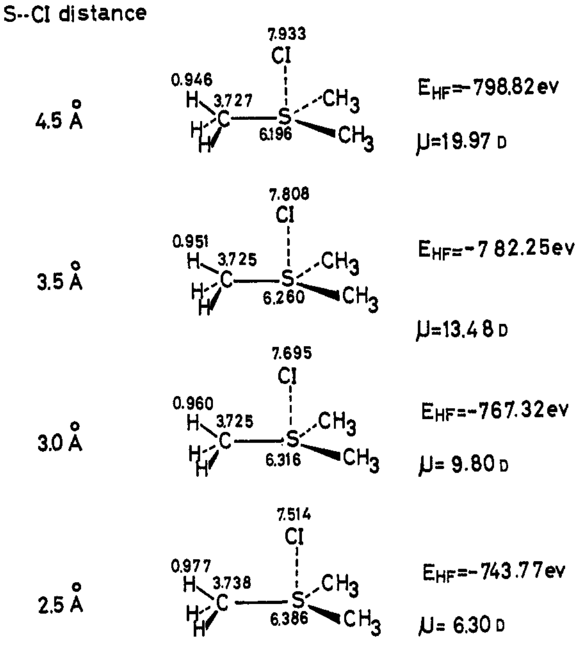

Figure 5.—The variation of the electronic state of $(CH_3)_3SCl$ with the bond distance of S–Cl.

As is shown in Figure 2, the lower polarity of solvents decreases the transition energies of this excitation $[(3p_z)^2 \rightarrow (3p_z)(3d)]$. Water, ethyl alcohol, and isopropyl alcohol gave the transition energy of 6.39, 6.08, and 5.97 eV in a nitrogen atmosphere, respectively (and of 6.37, 5.93, and 5.79 eV in an oxygen atmosphere, respectively); namely, the decrease of the polarity of a solvent shifted the transition to longer wavelengths. It is of interest and necessary, here, to consider the order of the stabilization by polar solvents. A rough approximation of the stabilization energy (ΔE_s) can be expressed by the equation, $\Delta E_s = e^2 \cdot (1 - 1/\epsilon)/2a$, where a is the ion radius of the salt (a is assumed to be 5 Å in this case) and ϵ is the dielectric

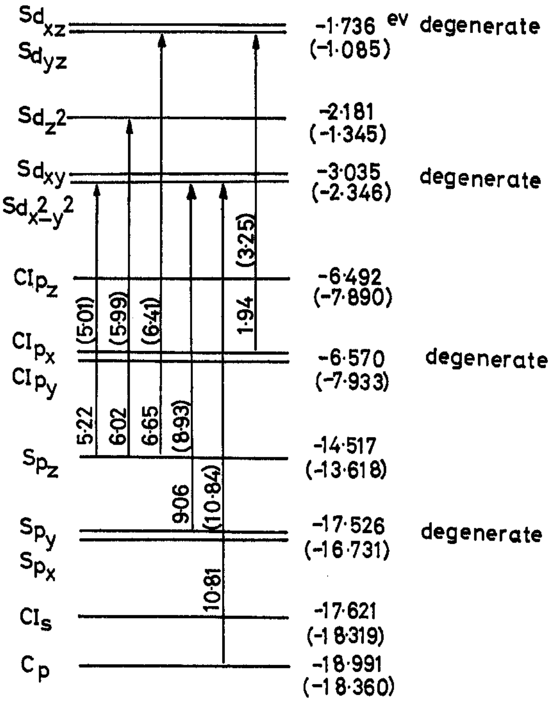

Figure 6.—Excitation energy of trimethylsulfonium chloride in ionic structure (S–Cl = 4.5, 3.5 Å). Values in the parentheses were those obtained from the ASMO–SCF calculation at S–Cl = 3.5 Å.

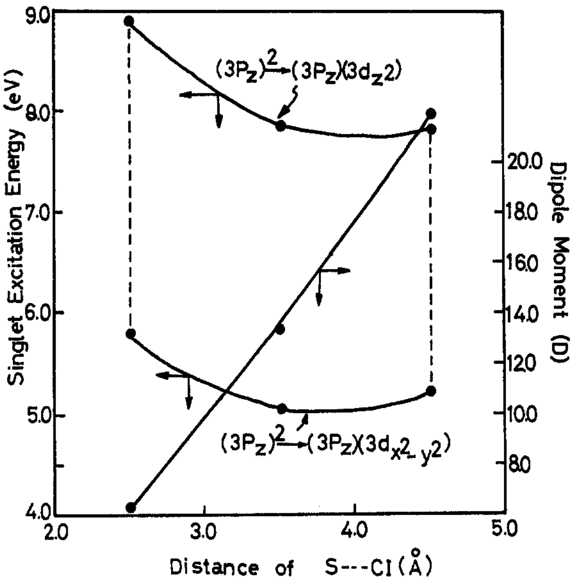

Figure 7.—Dependencies of the excitation energy and the dipole moment upon the S–Cl distance.

constant of the solvent.[43] In this case, the stabilization energy means the interaction energy between the sulfonium cation and the polar molecules, and hence the stabilization energy is considered to relate the electron density on the d sulfur orbital. It may be deduced, therefore, that the more electron density of the d sulfur orbitals increases, the higher its energy level becomes when the transition occurs; namely, the larger excitation energy is required for the transition, probably because of the electron repulsion on the d orbital by the partially occupying electron and of the screening of the nuclear charge by them. From these concepts, it may

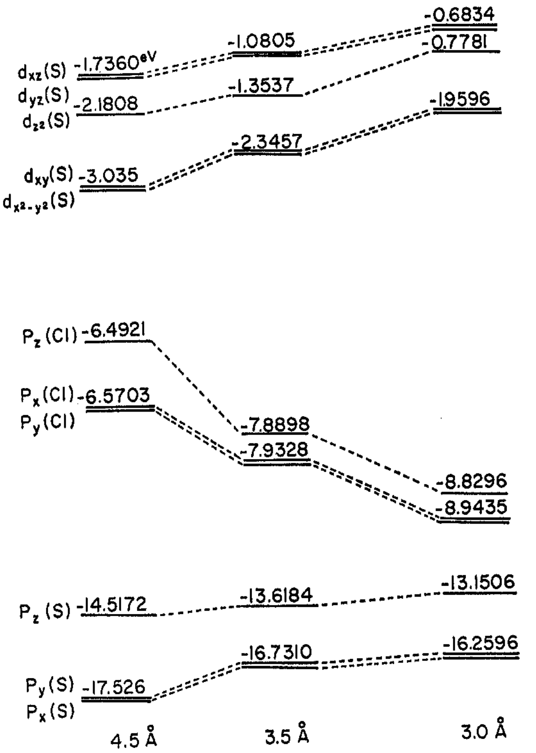

Figure 8.—An energy diagram in the bond length of S–Cl at 3.0–4.5 Å.

be concluded that the transition energy increases with the increase in the polarity of the solvents and hence with that in the stabilization energy. The calculated ΔE_S of water, ethyl alcohol, and isopropyl alcohol which is in the order of 1.46, 1.42, and 1.39 eV, respectively, well explains the tendency of the shifts of the transition energies.

It is found that the counteranion of the sulfonium influences this red shift to some extent (see Table IV). This suggests that, even in polar solvents, the dp–π or dp–σ bond nature[44] between the anion and the sulfonium cation is participated somewhat in the partially occupied nature[14] of d orbitals of the central sulfur, which relates directly to the excitation energy of the transition, $(3p_z)^2 \rightarrow (3p_z)(3d)$.

Neglecting the solvent effect on the transition energy, ASMO–SCF calculation of the singlet excitation energy of trimethylsulfonium chloride afforded the tendency of the decrease in the transition energy with the increase in the distance between the central sulfur and the chloride counteranion. As is shown in Figure 7, the dipole moment of the sulfonium salt is closely connected with the partial occupation of d orbitals[19] in the central sulfur, and the increase of dipole moment may argue the vacancy of the d sulfur orbital. These results are not contradictory to the considerations discussed above.

The energetic state relating to the transition of the central sulfur, $(3p_z)^2 \rightarrow (3p_z)(3d)$, is illustrated also in Figure 8. From the results obtained by ASMO–SCF calculations, however, it may be concluded that, in the presence of the solvent, in particular, of markedly polar solvents, the effect of the anion part is not so dominant.

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(43) J. Jortner, *J. Radiat. Res., Suppl.*, **4**, 24 (1964); J. Jortner and S. A. Rice, *Advan. Chem. Ser.*, **50**, 7 (1965).

(44) In the case of $(C_6H_5)_3SCl$, the dp–π bond nature is constructed by a bonding orbital [d_{yz}– (or d_{xz}–) orbital of sulfur atom and p_y– (or p_x–) orbital of Cl], and the dp–σ one is by an antibonding orbital [d_{z^2}– (or p_z–) orbital of sulfur atom and p_z– (or d_{z^2}–) orbital of Cl].

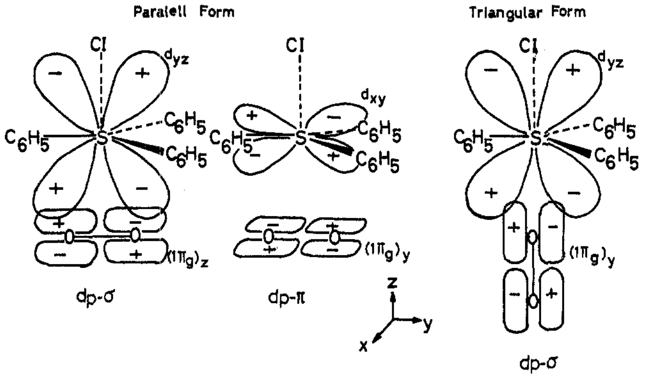

Figure 9.—Probable overlap between the sulfur and oxygen molecule.

The change of the energy level of the lone pair $(3p_z)^2$ orbital of the central sulfur atom caused by the solvents is considered to be little as compared with that of the d sulfur orbital. The above discussion of the central sulfur atom will be quite valid for the cases of different central atoms such as Se and Te. As shown in Figure 3, the excitation energy may not be so different from that of the sulfur atom.

Effect of Oxygen Molecule.—In an oxygen atmosphere, the oxygen molecule affected the shift of the transition energy, $(3p_z)^2 \rightarrow (3p_z)(3d)$, in the solvent directly, and the red shift caused by the oxygen molecule was 0.0, 0.15, and 0.18 eV in water, ethyl alcohol, and isopropyl alcohol, respectively. Namely, the decrease of the polarity of solvent shifts the spectrum to the red side. In a not so polar solvent such as ethyl alcohol or isopropyl alcohol, the vacant d orbital is considered to be occupied partially by electrons migrating from the anion part. When the oxygen molecule approaches to the sulfonium in such a circumstance, it may interact easily with the d orbital through the plausible overlapping as is shown in Figure 9.

Through the interaction, the partially occupied electron may be rather withdrawn to the orbital of the oxygen molecule, which causes the red shift of the transition as previously discussed (see Figure 10). Comparing the results of the spectra of S, Se, and Te, it is of interest that the red shift caused by the presence of the oxygen molecule was found to relate closely to the catalytic activity of onium salt in oxidation reaction.[19] Present experiments afforded the following results.

(a) Triphenyl-, alkyldiphenyl-, and trialkylsulfonium salts in polar solvents filled with gaseous nitrogen exhibit a narrow absorption band with fairly high intensity (log $\epsilon \sim 4$) in the neighborhood of 200 mμ [viz., 215 (5.77) $\sim$ 195 mμ (6.36 eV)]. In this case, the counteranions of sulfonium salts affect little the absorption band of the above range. This fact suggests that the band is not assigned to the charge-transfer band between the anion and the cation.

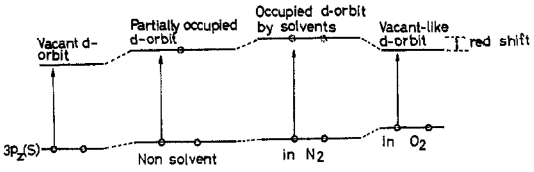

Figure 10.—A model of the energy change in the transition, $(3p_z)^3 \rightarrow (3p_z)(3d)$.

(b) Singlet excitation energy of trimethylsulfonium chloride which was constituted in the ionic configuration calculated by the ASMO–SCF method gave values of 5.22–6.65 eV for the transition of nonbonding $(3p_z)^2$ to $(3p_z)(3d)$.

(c) Molecular oxygen dissolved to a saturation in the solvent used shifted the band near 200 mμ to longer wavelengths and the red shift was *ca.* 0.25 eV at the utmost. The red shift was influenced by the temperature and the solvent used. The charge-transfer band, however, was not recognized anywhere. Lower temperatures promoted the red shift. This may mean the enhancement of the interaction between the sulfonium salt catalyst and molecular oxygen at lower temperatures as was discussed in a previous report.[21]

(d) The decrease of the dielectric constants of the solvent used allowed the $(3p_z)^2 \rightarrow (3p_z)(3d)$ transition at the lower energy region in the spectra in a nitrogen atmosphere and also in an oxygen atmosphere. The smaller the dielectric constant was, the more red shift was observed in the spectra.

(e) The fourth or fifth row elements in the periodic table of the onium central atom also showed the similar characteristic absorption spectra and the red shift in the presence of oxygen, the order of which was $(C_6H_5)_3SCl > (C_6H_5)_3SeCl > (C_6H_5)_3TeCl$.

Registry No.—$(CH_3)_3SBF_4$, 676-88-0; $(n\text{-}C_4H_9)_3SBF_4$, 14264-06-3; $(CH_3)_2(n\text{-}C_4H_9)SBF_4$, 31385-46-3; $(CH_3)_3SBr$, 3084-53-5; $(CH_3)_3SI$, 2181-42-2; $(C_6H_5)_3SCl$, 4270-70-6; $(C_6H_5)_3SeCl$, 6158-73-2; $(C_6H_5)_3TeCl$, 31426-14-9; $(C_6H_5)_3S \cdot {}^1/_3PO_4$, 22545-42-2; $C_{12}H_{10}SBF_4Ag$, 23733-42-8; $CH_3(C_9H_5)_2SBF_4$, 10504-60-6; $n\text{-}C_4H_9(C_6H_5)_2SBF_4$, 10504-61-7; $C_{12}H_{10}O_4SClAg$, 31426-16-1; Ph_3SBF_4, 437-13-8; $MeSPh_2ClO_4$, 10504-64-0; $EtSPh_2BF_4$, 893-69-6; $PrSPh_2BF_4$, 14264-05-2; $n\text{-}BuSPh_2ClO_4$, 10504-66-2.

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