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Reversible Oxygen Transfer Reactions between Sulfoxides and Sulfides. Relative Stabilities of Acyloxysulfonium Ions

Rikuhei TANIKAGA,* Koji NAKAYAMA, Kazuhiko TANAKA, and Aritsune KAJI
Department of Chemistry, Faculty of Science, Kyoto University Kitashirakawa, Sakyo-ku, Kyoto 606

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Synopsis. Sulfides and acyloxysulfonium ions generated from sulfoxides and trifluoroacetic anhydride undergo a reversible reaction at −80 °C. The acyloxysulfonium ions with electron-donating groups or less bulky groups were found to be more stable than those having electronwithdrawing or bulky substituents.

Intermolecular oxygen transfer reactions are known to occur between sulfoxides and sulfides. For example, the reaction between thiolane 1-oxide and dibenzyl sulfide in refluxing acetic acid gives dibenzyl sulfoxide,[1] and the refluxing of diaryl sulfides in dimethyl sulfoxide affords the corresponding sulfoxides in good yields.[2] Oae investigated an intramolecular oxygen migration reaction of *o*-(alkylthio)phenyl aryl sulfoxides in sulfuric acid, and proposed a mechanism involving the nucleophilic attack of the sulfide sulfur atom on the acyloxysulfonium sulfur atom.[3] Recently, we found a rapid reaction between sulfoxides and dimethyl sulfide in trifluoroacetic anhydride (TFAA), which can be applied for the convenient reduction of sulfoxides to the corresponding sulfides.[4] Interestingly, dimethyl sulfoxide is an oxidizing agent in one case, while dimethyl sulfide is a reducing agent in the other case. However, no reversible oxygen transfer reaction between sulfoxides and sulfides has yet been studied.

In extending our observation, we have studied the reversible oxygen transfer reactions between various sulfoxides and sulfides using TFAA, and determined the relative stabilities of acyloxysulfonium ions which had not been estimated.

Experimental

The NMR spectra were recorded on a JEOL PS-100 spectrometer. GLPC determination was performed on a Varian 920 apparatus, using 1.2 m×6 mm column packed with 20% Silicone DC-550 on 40—60 mesh Celite support. Sulfoxides and sulfides employed were prepared by the known methods. Dichloromethane and acetonitrile were distilled over CaH_2 and P_2O_5, respectively. Commercially available TFAA was used without further purification.

Typical Procedure. A solution of TFAA (12 mmol) in dichloromethane (5 ml) and acetonitrile (5 ml) was added dropwise to a solution of methyl phenyl sulfoxide (**1f**, $R=CH_3$, $R'=C_6H_5$) (1.40 g, 10 mmol) and ethyl phenyl sulfide (**4**) (1.38 g, 10 mmol) in dichloromethane (10 ml) and acetonitrile (10 ml) during 5 min at −80 °C, and the mixture was stirred for 90 min. After addition of a small amount of aq NaOH, the mixture was stirred for 5 min at −80 °C and allowed to warm to room temperature. A saturated NaCl solution (50 ml) was added, the layers were separated, and the aq phase was washed with two 30 ml portions of dichloromethane. The combined organic phase was washed with aq $NaHCO_3$ and water, and dried over $MgSO_4$. Evaporation of the solvent gave a liquid (2.7 g). TLC GLPC revealed that the liquid contained four compounds: that is, **1f**, methyl phenyl sulfide (**2f**), ethyl phenyl sulfoxide (**3**), and **4**. No other compound was detected in the NMR spectrum of the liquid. The relative yield of each compound was determined by GLPC and NMR using the authentic samples: **2f**/**4**=53/47, and **3**/**1f**=53/47.

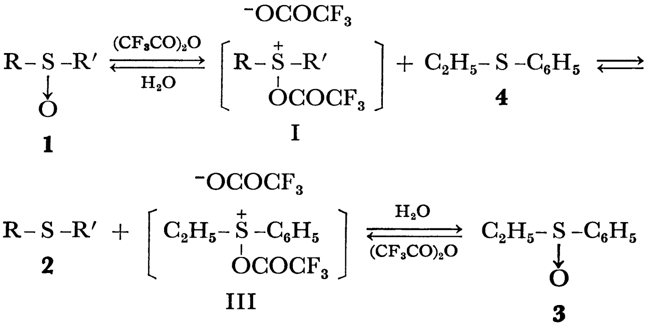
In order to determine whether quenching with aq NaOH was complete in 5 min at −80 °C, dimethyl sulfide (1.24 g, 20 mmol) was added to the mixture at −80 °C after stirring with aq NaOH for 5 min, but **1f**, **2f**, **3**, and **4** were obtained in the same yields as above.

Following a similar procedure, **2f**/**4**=51/49 was obtained from **2f** and **3**.

Results and Discussion

Since sulfoxides (**1**) were instantaneously reduced to sulfides (**2**) with TFAA and dimethyl sulfide at −80 °C,[4] the formation of acyloxysulfonium ions (I) from **1** is assumed to be very rapid and quantitative. When TFAA was added to a solution of **1f** in dichloromethane and acetonitrile at −80 °C, and after 90 min the reaction mixture was quenched with aqueous NaOH, **1f** was recovered quantitatively. This finding means that **1** never underwent the Pummerer rearrangement at −80 °C.

When TFAA was added to a solution of **1f** and **4** at −80 °C, and after 90 min the mixture was quenched with aqueous NaOH at −80 °C, **1f**, **2f**, **3**, and **4** were obtained, but no other product was detected. Upon similar treatments, **1f**, **2f**, **3**, and **4** were also obtained from **2f** and **3** in nearly the same yields. The relative yields of **2f**/**4** were found to be nearly equal to those of **3**/**1f**, suggesting that the following equilibrium exists:



$$\underset{\mathbf{1}}{R-\underset{\downarrow\atop O}{S}-R'} \underset{H_2O}{\overset{(CF_3CO)_2O}{\rightleftarrows}} \underset{\mathrm{I}}{\left[R-\overset{+}{\underset{|\atop OCOCF_3}{S}}-R'\right]^{-}OCOCF_3} + \underset{\mathbf{4}}{C_2H_5-S-C_6H_5} \rightleftarrows$$

$$\underset{\mathbf{2}}{R-S-R'} + \underset{\mathrm{III}}{\left[C_2H_5-\overset{+}{\underset{|\atop OCOCF_3}{S}}-C_6H_5\right]^{-}OCOCF_3} \underset{(CF_3CO)_2O}{\overset{H_2O}{\rightleftarrows}} \underset{\mathbf{3}}{C_2H_5-\underset{\downarrow\atop O}{S}-C_6H_5}$$

f $R=CH_3$, $R'=C_6H_5$

If **If** and III were not quenched within a few minutes at −80 °C, dimethyl sulfide would rapidly react with **If** and III to give **2f** and **4**, but not to give **1f** and **3**.[4] The addition of dimethyl sulfide during quenching, however, did not affect the yields of the products.

A NMR spectrum of **1f**, **4**, and TFAA (mol ratio: 1.0: 1.0: 1.2) in CH_2Cl_2–CD_3CN (v/v=1/1) at −80 °C showed peaks at 2.7, 2.4, 1.2, 1.1 ppm corresponding to the methyl groups of **If**, **2f**, III, and **4**, respectively. Although the relative yields of **2f**/**4** could not be determined because of overlapping of two methyl signals of III and **4**, those of **2f**/**If** were found about 50/50.

The above findings mean that the III/**If** ratio would be essentially the same as the **3**/**1f** (or **2f**/**4**) ratio.

The conceivable pathway from I and **4** to **2** and III (and *vice versa*) may involve the nucleophilc attack of the sulfide sulfur atom on the sulfonium sulfur atom.[3–5]

The results obtained with other sulfoxides, and **4**, are shown in Table 1.

TABLE 1. RELATIVE YIELDS OF **2**/**4** FROM **1** AND **4** (OR **2** AND **3**)

	R	R′	Yield ratio (**2**/**4**)
a	CH_3	CH_3	0/100
b	CH_3	n-C_6H_{13}	2/98
c	CH_3	p-CH_3O-C_6H_4	36/64
d	CH_3	p-CH_3-C_6H_4	47/53
e	CH_3	o-CH_3-C_6H_4	66/34
f	CH_3	C_6H_5	53/47
g	CH_3	p-Cl-C_6H_4	76/24
h	CH_3	o-Cl-C_6H_4	94/6
i	CH_3	p-NO_2-C_6H_4	100/0
j	i-C_3H_7	C_6H_5	54/46
k	CH_2Cl	C_6H_5	100/0
l	C_6H_5	C_6H_5	99/1

Since the above equilibrium is considered to depend on the relative stabilities of the acyloxysulfonium ions I and III, the smaller **2**/**4** ratio means that I is more stable. On this basis, the relative thermodynamic stabilities of I can readily be determined. Thus, we may reasonably conclude that an electron-donating group can make I more stable, and the steric bulkiness, for example, of an *o*-substituent makes I slightly unstable. The former conclusion also suggests that I obtained from basic **1** must be stable. In fact, the stabilities of I were found qualitatively to parallel the pK_a values of **1**,[6] though attempts to find out the exact relationships between them were unsuccessful.

The position of the equilibrium was little affected by the presence of 2,6-lutidine. The time necessary to attain the equilibrium varied from a few seconds (*i.e.*, from **2a** and **3**) to a few hours (*i.e.*, **1i** and **4**).

Since dimethyl sulfoxide forms the most stable acyloxysulfonium ion, other sulfoxides can be reduced with dimethyl sulfide in TFAA.[4] The intramolecular oxygen migration of *o*-alkylthiophenyl aryl sulfoxides also showed that alkyl(aryl)(oxy)sulfonium ions are more stable than diaryl(oxy)sulfonium ions.[3] When one component is removed in the equilibrium, the equilibrium can be displaced to the unfavorable direction. This is the case of the oxidation of sulfides with dimethyl sulfoxides.[2]

When trichloroacetic anhydride, trichloroacetyl chloride, and thionyl chloride were used in the place of TFAA, the **3**/**1** yield ratios were found to be 56/44, 55/45, and 55/45, respectively, and the order of the relative stabilities of the oxysulfonium ions was identical to that obtained with TFAA. When dichloroacetic anhydride was used, it took a much longer time to reach the equilibrium. No intermolecular oxygen exchange reaction of a sulfoxide and a sulfide took place in sulfuric acid at room temperature, or in acetic anhydride at 100 °C, unlike the intramolecular reaction.[3] Evidently such a decrease in reactivities corresponds to a decrease in the leaving group tendency; for example, $CF_3COO^- > CCl_3COO^- > CHCl_2COO^- > CH_3COO^-$.

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