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Oxosulfonium Salts. II. Nitration of Dimethylphenyloxosulfonium Salt

Kenji Kamiyama, Hiroshi Minato, and Michio Kobayashi
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo 158

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The effects of the positively charged substituents of arenes on the rates and isomer distributions in electrophilic aromatic substitution have been studied by various investigators. In connection with the question whether or not the pπ—dπ resonance exists between aromatic rings of aryl onium salts and the positively charged hetero atoms, electrophilic aromatic substitution of anilinium salts[2] and onium salts of some hetero atoms involving d-orbitals (P, Se, As, and S)[3] have recently been reported. In the substitution reaction of the aryl onium salts of selenium and sulfur the ortho and para substituted products were found in considerable yields, and the existence of pπ—dπ resonance was proposed in these cases.[4–6]

Oxosulfonio groups, $-\underset{\overset{\|}{O}}{\overset{\oplus}{S}}R_2$, are expected to be more strongly electron-withdrawing than sulfonio groups, $-\overset{\oplus}{S}R_2$. Studies on aromatic substitution of $Ar\underset{\overset{\|}{O}}{\overset{\oplus}{S}}R$ would yield useful information on the presence or absence of resonance between the aromatic ring and the tetrahedral sulfur atom of an oxosulfonio group. Although alkyloxosulfonium salts are fairly reactive with nucleophilic agents and act as methylating agents of thiolate or hydroxide ions, they are very stable toward oxidizing agents and electrophiles. Therefore, it is possible to investigate the electrophilic substitution on oxosulfonio-arenes. However, the electrophilic substitution of aryl oxosulfonium salts has not been reported in the literature, because the preparation of aryl oxosulfonium salts is rather difficult.

In order to determine the electronic effect of oxosulfonio groups on electrophilic aromatic substitution, the nitration of dimethylphenyloxosulfonium salt has been investigated.

Results and Discussion

Product Study. Dimethylphenyloxosulfonium perchlorate (I) remained unchanged when it was heated in concd nitric acid at 70 °C. When a solution of I in a mixture of concd sulfuric acid and fuming nitric acid (*d*, 1.52) (*v*/*v* 2/1) was heated at 80 °C for 3 hr, dimethylnitrophenyloxosulfonium perchlorate (II) was obtained in 80—87% yield. When II was refluxed in a solution of sodium iodide in acetone and the sulfoxide (III) obtained was oxidized to the corresponding sulfone, only the *m*-nitro isomer was found. No *ortho* and *para* isomer were detected with a flame-ionization gas chromatography.

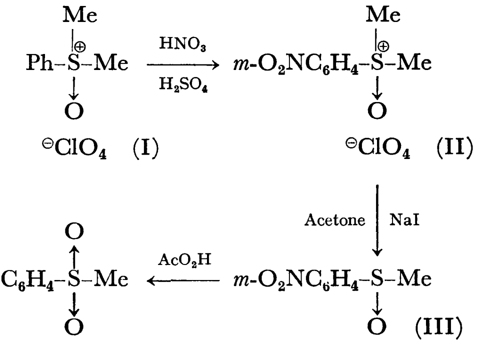
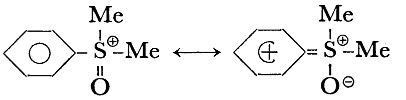


Table 1. Isomer distribution in the nitration of some aromatics possessing positive poles

Aromatics	Nitro-aromatics *ortho*%	*meta*%	*para*%	Reference
$Ph\overset{\oplus}{N}Me_3$	0	89	11	7)
$Ph\overset{\oplus}{P}Me_3$	0	97	3	7)
$Ph\overset{\oplus}{As}Me_3$	0	96	4	7)
$Ph\overset{\oplus}{Se}Me_2$	2.6	91.3	6.1	4)
$Ph\overset{\oplus}{S}Me_2$	3.6	90.4	6.0	4)
	2.18	93.87	3.95	6)
$PhMe_2\overset{\oplus}{S}{=}O$	0	100	0	This work

The results are shown in Table 1 together with the data on nitration of other onium salts. The nitration of dimethylphenylsulfonium ion gave the *o*- and *p*-nitro derivatives in 5—10% yields, whereas that of dimethylphenyloxosulfonium ion gave no *o*- and *p*- derivatives.

The stretching frequencies of S–O of *p*-substituted phenyldimethyloxosulfonium ions were found to be proportional to the Hammett σ^+ values;[8] this finding suggests a 2p—3p resonance between the benzene ring and the S=O bond.



The fact that only *m*-nitro product was formed in nitration of I is ascribable to the inductive effect of the dimethyloxosulfonio group but also the resonance des-

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[1] Organic Sulfur Compounds. Part XXXVIII.

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[6] N. C. Marziano, E. Maccarone, and R. C. Passerini, *Tetrahedron Lett.*, **1972**, 17.

[7] J. H. Ridd and J. H. Utley, *Proc. Chem. Soc.*, **1964**, 24.

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cribed above. In order to ascertain this, the kinetics of nitration was also investigated.

Kinetic Study. Nitration of I in a mixture of 98% H_2SO_4 and fuming HNO_3 (*d*, 1.52) (*v*/*v*, 2/1; $[HNO_3]=8.23$ M) was followed by the increase of the UV absorption at 250 nm ascribable to II. (λ_{max} of II, 250 nm, $\varepsilon_{II}=7.063$; ε_I at 250 nm is 328). The reaction was first order in I, and good linear relationship was observed. The rate constants obtained are shown in Table 2.

Table 2. The rate constants of nitration of I in concd H_2SO_4

Temperature (°C)	$10^5 \times k$ (M^{-1} sec^{-1})
40.0	0.917±0.04
50.0	2.11 ±0.06
60.0	4.30 ±0.06

Table 3 compares the rate parameters of nitration of I and dimethylphenylsulfonium ion in concentrated sulfuric acid. The rate of nitration of I is very much smaller than that of the sulfonium ion (by a factor of 500), and this smaller rate is ascribable to the greater activation energy. These data show that the benzene ring of I is considerably deactivated because of the 2p—3p resonance between the ring and the $-\overset{\oplus}{S}(=O)Me_2$.

Very small rates of nitration of I suggest that the σ-value of an oxosulfonio group is very large. When the σ_m-value of $-\overset{\oplus}{S}(=O)Me_2$ was calculated from the rates of nitration at *meta* and *para* positions of $Ph\overset{\oplus}{N}Me_3$, $Ph\overset{\oplus}{S}Me_2$, and $PhMe_2\overset{\oplus}{S}{=}O$, 1.38±0.04 was obtained. This σ-value is the greatest among the σ values known except the values for diazonium ion $-\overset{\oplus}{N}_2$ (σ_m 1.76; σ_p 1.91),[9] and much greater than σ_m of $-\overset{\oplus}{N}Me_3$ (1.01) and $-\overset{\oplus}{S}Me_2$ (1.00). The diazonium group is unstable and reactive whereas the oxosulfonio group is stable and much less reactive. Therefore, the oxosulfonio groups are expected to be very useful for the studies on the effects of substituents on various organic reactions or the properties of various organic compounds.

Experimental

Preparation of Dimethylphenyloxosulfonium Perchlorate (I). After a mixture of mercury(II) iodide (20 g, 44 mmol) and methyl iodide (30 ml) was deaerated in a 100 ml flask by bubbling nitrogen, it was stirred with a magnetic stirrer for 30 min under nitrogen. Then methyl phenyl sulfoxide (20 g, 142 mmol) was added, and the mixture was refluxed for 65 hr. When the excess methyl iodide was removed by distillation and the unchanged sulfoxide was removed by extraction with ether, reddish brown residue was obtained, which crystallized when extraction with ether was repeated few more times. Recrystallization from methanol gave light yellow leaflets of dimethylphenyloxosulfonium mercuritriiodide; yield, 14.0 g; mp 138—139 °C (decomp.); IR, 1230, 750 cm^{-1}; NMR (acetone-d_6), δ, 4.43 (s, 6H), 8.27 (m, 5H).

Table 3. Activation parameters for nitration of sulfonium and oxosulfonium salts in concd H_2SO_4

	E_a (kcal/mol)	ΔS (e.u.)	$10^5 k_{25°C}$ (M^{-1}sec^{-1})	$10^6 k_{0.5°C}$ (M^{-1}sec^{-1})
$Ph\text{-}\overset{\oplus}{S}Me_2$	12.9	−28.0	133[a]	150[b]
$Ph\text{-}\underset{\underset{O}{\|}}{\overset{\oplus}{S}}Me_2$	16.0	−32.4	0.245	0.218[c]

a) Ref. 6.

b) Determined in the mixed acid used for nitration of $PhMe_2\overset{\oplus}{S}{=}O$

c) Calculated by use of E_a.

The mercuritriiodide salt (22.2 g) was dissolved in acetone (200 ml), and an acetone solution of silver perchlorate was added until no more precipitates (AgI, HgI_2) were formed. After the precipitates were filtered off, the acetone was removed under reduced pressure. When the residue was recrystallized from methanol several times, I was obtained as white needles; yield, 5.5 g (73%); mp 158—159 °C; IR, 1230 (ν_{S-O}), 1100, 750 cm^{-1}. Found: C, 37.67; H, 4.31%. Calcd for $C_8H_{11}O_5SCl$: C, 37.71; H, 4.35%.

Measurements of the Rates of Nitration of I. A mixture of 98% sulfuric acid and fuming nitric acid (*d*, 1.52) (v/v= 2/1) was used. The concentration of HNO_3 was 8.23 M. A solution of I (about 1 mmol) in the mixed acid (10 ml) was placed in a constant temperature bath, and the samples withdrawn after suitable intervals were diluted with water (1000 times by volume), and the UV absorptions were determined against the reference (the mixed acid diluted by the same factor).

Identification of the Product of Nitration of I. After a mixture of I (318.4 mg), 98% sulfuric acid (2 ml) and fuming nitric acid (1 ml) was heated at 80.0 °C for 3 hr, it was diluted with ice water (20 ml), and the crystals formed were filtered. When the filtrate was made weakly alkaline and an aqueous $NaBPh_4$ solution was added, $O_2NC_6H_4\overset{\oplus}{S}(=O)Me_2\ Ph_4\overset{\ominus}{B}$ precipitated. The total amount of II isolated (the crystals plus the tetraphenylborate salt obtained from the filtrate) amounted to 87%. Dimethylnitrophenyloxosulfonium perchlorate. Found: C, 32.13; H, 3.40; N, 4.85%. Calcd for $C_8H_{10}O_7ClNS$: C, 32.03; H, 3.36; N, 4.68%.

After the nitrated salt was refluxed in an acetone solution (40 ml) of sodium iodide (0.435 g) for 2 hr, the acetone was removed under reduced pressure, and the residue obtained was heated with 30% hydrogen peroxide (2.0 g) and acetic acid (5 ml) at 70—90 °C for 2 hr. Then the solution was diluted with water, and extracted with dichloromethane. The extracts combined were concentrated, and the residue was subjected to gas-chromatographic analysis (a Hitachi K-51 Gas Chromatograph; column, Silicone XF 1105 on Chromosorb W, 2 m).

Determination of Rates of Nitration of Dimethylphenylsulfonium Perchlorate. In 10.0 ml of the mixed acid used for the nitration of I, about 1 mmol of dimethylphenylsulfonium perchlorate was dissolved, and the mixture was let to react in a constant temperature bath. After suitable intervals, samples were withdrawn and diluted with water (1000 times by volume). The rate constant was calculated from the increase of the UV absorptions at 256 nm (ε of dimethylphenylsulfonium salt is 555, whereas that of the nitrated salt is 7256).[5]

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[9] E. S. Lewis and M. D. Johnson, *J. Amer. Chem. Soc.*, **81**, 2070 (1959).