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MULTISTEP OXIDATIONS OF THE UNSYMMETRICAL DISULFIDE AND THIOLSULFINATES: NEW EVIDENCE FOR THE FORMATION OF THE THIONITRITE AND THE SULFINYL DERIVATIVES AS THE INTERMEDIATES

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The oxidations of unsymmetrical disulfide and thiolsulfinates with excess dinitrogen tetraoxide afforded the corresponding symmetrical thiolsulfonates as the main product. The oxidation was found to involve the formations of intermediates of the thionitrite and the sulfinyl nitrite or the sulfinyl nitrate, which are undoubtedly formed by the fission of S-S bond.

Although there have been a few interesting works on the oxidations of disulfides with dinitrogen tetraoxide (N_2O_4)[1], no systematic study on the mechanism of the oxidation has been reported. Symmetrical disulfides were known to be oxidized with excess N_2O_4 to the corresponding sulfonic anhydrides in good yields[1]. One puzzling question is whether the oxidation undergoes via a stepwise process like that by organic peroxy acid or via a multistep route like in the case of ozonization, which involves the cleavage of sulfur-sulfur bond. During the studies on the oxidations of unsymmetrical disulfides, we have found that the oxidation of methyl phenyl disulfide (1) or S-phenyl methanethiosulfinate (2) undergoes via forming the unstable intermediates, i,e. the thionitrites (I,II) and sulfinyl nitrite or sulfinyl nitrate (III), which are undoubtedly derived by the cleavage of sulfur-sulfur bond of the substrates.

When (1)~(3)(0.5 mmol, CCl_4:20 ml) were oxidized with N_2O_4 at 0°C, the corresponding symmetrical thiolsulfonates, disulfides and sulfonic acids were obtained. The results are shown in Table I.

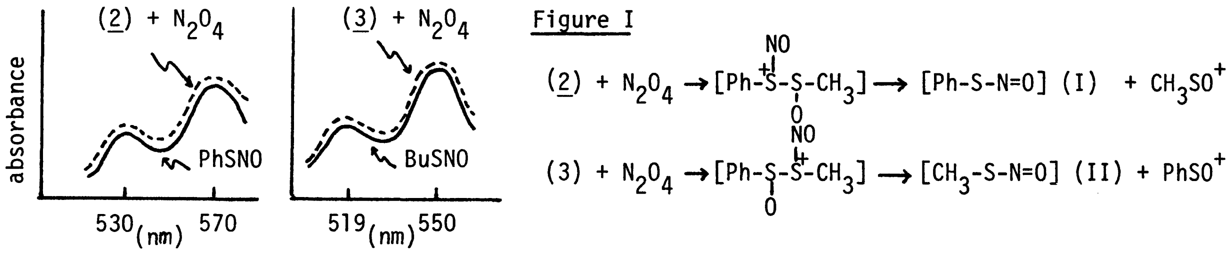
Table I. Oxidation of Unsymmetrical Disulfide and Thiolsulfinates

Substrate	N_2O_4(mmol)	Reaction time(min)	Products (mol %)				
			PhSSPh	$PhSS(O)_2Ph$	$PhSO_3H$	$CH_3SS(O)_2CH_3$	CH_3SO_3H
$Ph\text{-}S\text{-}S\text{-}CH_3$ (1)	1.0	120	18.5	20	20	2.5	49
$Ph\text{-}S\text{-}S(O)\text{-}CH_3$ (2)	0.6	60	0	45	trace	2.5	50
$Ph\text{-}S(O)\text{-}S\text{-}CH_3$ (3)	0.6	30	trace	trace	85	2.5	45

During the oxidation of (1), formation of the intermediate monoxide (2) was detected by comparing the UV spectra of the reaction mixture with that of the authentic sample by HPLC*. However, S-methyl benzenethiosulfinate (3) could not be detected. Probably the electron rich sulfur atom attached to the methyl group is more readily oxidized than the other to afford the thiolsulfinate (2). The product distribution shown in Table I also suggested strongly that the thiolsulfinate (2) is an intermediate; main products are S-phenyl benzenethiosulfonates and methanesulfonic acid in the cases of (1) and (2) in contrast to the case of (3); namely the main products are the sulfonic acid. All these symmetrical products and sulfonic acids were undoubtedly derived from the scission of sulfur-sulfur bond.

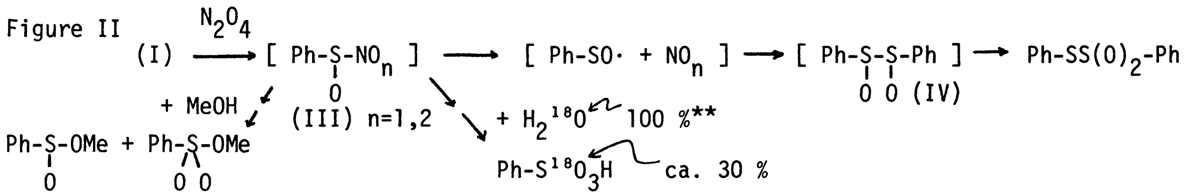
In order to search for other intermediates formed by sulfur-sulfur cleavage, the first intermediate, the thiolsulfinate (2) was oxidized with a diluted N_2O_4 solution ((2): 0.1 mmol in 5 ml of CCl_4, N_2O_4: 0.01 mmol) in the UV cell at ca. 0°C in a cold room. New visible light absorptions (530 and 570 nm) were detected during the oxidation. This visible spectrum was identical to that of the authentic sample of S-phenyl thionitrite (Ph-S-N=O, Fig. I)[2]. The characteristic color change of the thionitrite was also observed in the reaction cell. Generally, S-alkyl thionitrites are known to be more stable than S-aryl thionitrites[2]. Therefore, for further evidence for the formation of the S-alkyl thionitrite intermediate, S-methyl benzenethiosulfinate (3) was treated in the same way and the formation of S-methyl thionitrite was detected by comparing the new absorption (---) with that of S-butyl thionitrite (—) (Fig. I)[3].

Figure I



Probably the electrophilic attack of NO^+ on the sulfenyl sulfur atom forms the thionitrites (I,II), which may rapidly be oxidized further to the sulfinyl nitrite or the sulfinyl nitrate (III). The unstable intermediates (III) would then be decomposed to the sulfinyl radicals, which readily dimerized to give α-disulfoxide (IV) upon recombination of the two sulfinyl radicals[4]. The α-disulfoxide has now been accepted as an important intermediate which is readily isomerized to the corresponding thiolsulfonate in the oxidation of (3) with AcO_2H[4].

Figure II



Evidence for the formation of the intermediates (III) may be obtained in the oxidation of the thionitrite (I) with excess of N_2O_4 at 0°C to afford III , which was then reacted with $H_2{}^{18}O$ and methanol. Indeed, the treatment of S-phenyl thionitrite solution (PhSH: 2.0 mmol, N_2O_4: 4.0 mmol) with methanol (ca. 50 mmol) afforded methyl benzenesulfinate (19 %), methyl benzenesulfonate (11 %) and the thiolsulfonate (41 %). Moreover, the same treatment of S-phenyl thionitrite with $H_2{}^{18}O$ gave benzenesulfonic acid (20 %), which contained ^{18}O-label of 29.6 % of that of water. These results suggested that the nucleophilic attack of methanol or $H_2{}^{18}O$ to the sulfinyl sulfur atom of (III) afforded these products. Incidentally, benzenesulfinic acid was readily oxidized to the sulfonic acid under the same condition and thus probably, the sulfinic acid ($PhS^{18}O_2H$) which formed by the reaction of (III) and $H_2{}^{18}O$ was oxidized further with excess N_2O_4 to the corresponding sulfonic acid.

References and Notes

1) N. Kunieda and S. Oae, Bull. Chem. Soc., Japan, 41, 233 (1968): G.W. Weinrich, Qurt. Rep. Sul. Chem., 2, 367 (1967) 2) S. Oae, D. Fukushima, and Y.H. Kim, J. Chem. Soc., Chem. Commn., 1977, 407 3) Since methyl thionitrite is gas, butyl thionitrite was prepared and used instead of it. 4) S. Oae, Y.H. Kim, T. Takata, and D. Fukushima, Tetrahedron Lett., 1195 (1977): M.M. Chau and J.L. Kice, J. Am. Chem. Soc., 97, 7711 (1976) *) high-pressure liquid chromatography **) 1.6 atom%

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