The Structures of Zincke's So-called o- and p-Nitrobenzenesulfenic Anhydrides

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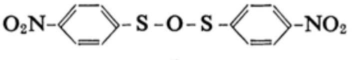
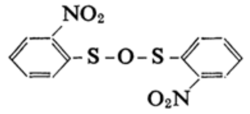
Zincke[1,2], in the neutral hydrolysis of *o*- and *p*-nitrobenzenesulfenyl chlorides, obtained compounds corresponding to $C_{12}H_8N_2S_2O_5$ and he then assumed these compounds to be the sulfenic anhydrides, I and II, respectively.



I



II

Much later Kharasch[3] has cited five more examples of similar anhydrides and presumed that they arise in the following fashion:

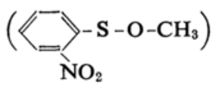
$$\mathrm{ArSCl} \xrightarrow{\mathrm{HOH}} [\mathrm{ArSOH}] \xrightarrow{\mathrm{ArSCl}} \mathrm{ArSOSAr}$$

All these compounds are known to darken or sinter before melting or decomposing.

We have interested in Zincke's so-called *o*- and *p*-nitrobenzenesulfenic anhydrides, since we thought these would be the ideal compounds for the determination of the bond length of sulfur-oxygen single bond which has hitherto been unknown. However, somewhat unexpected patterns of the ultraviolet and infrared spectra of both compounds have led us to suspect the authenticities of the structures of these compounds hitherto accepted.

The compound, obtained from the hydrolysis of *p*-nitrobenzenesulfenyl chloride, when recrystallized from benzene[1], has a distinct band in infrared region, i. e., 1145 cm^{-1} which corresponds either to sulfoxide or sulfone. Meanwhile, the compound corresponding to I, would display a strong band below 1000 cm^{-1} in view of other examples shown in Table I which indicates that the characteristic bands of Si-O-Si and of P-O-P are both similar or shifted slightly toward longer wavelengths as those of Si-O-C and of P-O-C.

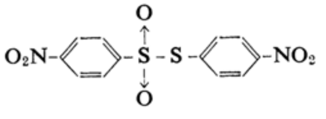
TABLE I*. CHARACTERISTIC BANDS OF ETHER LINKAGES OF SECONDS-ROW ELEMENTS

		cm^{-1}	
Si-O-C		1090∼1020	(s)
Si-O-Si	(ring)	1090∼1020	(s)
Si-O-Si	(chain)	1090∼1010	(s)
P-O-C	(aliphatic)	1050∼1030	(s)
P-O-C	(aromatic)	1240∼1190 (s) 1160 (w)	
P-O-P		970∼910	(s)
S-O-C		990	(s)

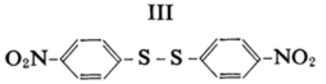
* About the spectra of six compounds except for the last methyl ether, for instance see the Ref. 4.

Since the oxygen exchange is known to take place in sulfuric acid with the sulfoxide but not with the sulfone[5] and also we found that nitrobenzene does not exchange oxygen in the same medium, we carried out the oxygen exchange experiment with the ^{18}O-enriched Zincke's compound in sulfuric acid. However, the compound recovered by diluting in water did not lose any excess of ^{18}O.

Infrared spectra of *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate (III) and *p,p'*-dinitrodiphenyl disulfide (IV) were then taken.



III



IV

When these spectra were compared with that of recrystallized Zincke's compound, we could find virtually all the bands of III and IV in Zincke's compound. When an equimolar mixture of III and IV was recrystallized from benzene, the resulting mixture, which could not be separated by ordinary recrystallization,

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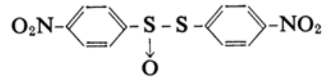
[1] T. Zincke and S. Lenhardt, *Ann.*, **400**, 1 (1913).
[2] T. Zincke and F. Farr, ibid., **391**, 55 (1912).
[3] N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **1947**, 327.
[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd Ed., Methuen, London (1958).
[5] S. Oae, T. Kitao and Y. Kitaoka, *Chem. & Ind.*, **1961**, 291.

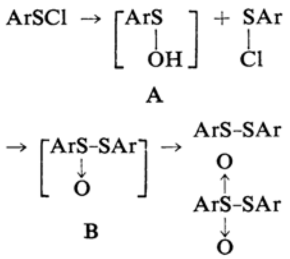
gave completely identical infrared and ultraviolet spectra with those of Zincke's compound. These results point to the fact that Zincke's so-called *p*-nitrobenzenesulfenic anhydride is actually an equimolar mixture of *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate (III) and *p*, *p*′-dinitrodiphenyl disulfide (IV).

In searching a possible intermediate in the hydrolysis of *p*-nitrobenzenesulfenyl chloride, we carried out the oxidation of *p*, *p*′-dinitrodiphenyl disulfide by perbenzoic acid, following the method of Backer[6] and Small[7], hoping to obtain *p*-nitrophenyl *p*-nitrobenzenethiolsulfinate (V). However, what we obtained was also an equimolar mixture of *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate (III) and *p*, *p*′-dinitrodiphenyl disulfide (IV).



V

In the meantime, fresh hydrolysis product of *p*-nitrobenzenesulfenyl chloride, when only washed with ether and quickly dried, gave a very strong band at 1118 cm^{-1} and darkened at about 123°C. When this fresh product was subjected to heating in vacuo, storing for a long time or recrystallization, it gradually ceased darkening before melting and lost the band at 1118 cm^{-1} while changing its ultraviolet spectrum. This band at 1118 cm^{-1} is close to that of *p*-tolyl *p*-toluenethiolsulfinate, 1094 cm^{-1}[8] and is likely to be that of thiolsulfinate but is shifted toward shorter wavelength on account of strong electron-attracting nitro groups. This means that the fresh hydrolysis product is likely to be *p*-nitrophenyl *p*-nitrobenzenethiolsulfinate (V), which subsequently disproportion to *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate (III) and *p*, *p*′-dinitrodiphenyl disulfide (IV) when the fresh product is recrystallized or kept standing for a while.



The consideration of *p*-nitrophenyl *p*-nitrobenzenethiolsulfinate (V) as an intermediate* is quite likely in view of the facts that many known thiolsulfinates are very unstable and disproportion easily to corresponding thiolsulfonates and disulfides[6] and also that the sulfur atom of A, being more nucleophilic than oxygen atom, would attack sulfenyl chloride in the second step of the hydrolysis giving B rather than the anhydride, I.

o-Nitrobenzenesulfenyl chloride, when hydrolyzed following Zincke's procedure[2] gave the product which was claimed to be the sulfenic anhydride. The fresh product had a strong band at 1108 cm^{-1}, corresponding to the thiolsulfinate band of *p*-isomer and also a medium band at 1145 cm^{-1} corresponing to that of thiolsulfonate. These bands subsisted even after repeated recrystallizations from benzene or heating in vacuo for a few hours, while the darkening point fluctuated up and down around 70°C on each batch. We tried similar oxidation of *o*, *o*′-dinitrodiphenyl disulfide with perbenzoic acid[6,7], hoping to obtain the thiolsulfinate. The reaction was very sluggish even under irradiating with ultraviolet light[9], and the only compound we could isolate was a small amount of the thiolsulfonate, recovering most of the starting material. We tried a few other attempts to synthesize the authentic *o*-nitrophenyl *o*-nitrobenzenethiolsulfinate in vain. When an equimolar mixture of *o*-nitrophenyl *o*-nitrobenzenethiolsulfonate and *o*, *o*′-dinitrodiphenyl disulfide was recrystallized from benzene and this mixture was compared with Zincke's compound, we found some small discrepancies in both ultraviolet and infrared spectra, while the melting point also did not show identity. However, we found that Zincke's compound has all the infrared bands of the equimolar mixture of *o*-nitrophenyl *o*-nitrobenzenethiolsulfonate and *o*, *o*′-dinitrodiphenyl disulfide in addition to the characteristic band at 1108 cm^{-1}. This seems to indicate that Zincke's so-called *o*-nitrobenzenesulfenic anhydride is the mixture of *o*, *o*′-dinitrodiphenyl disulfide, *o*-nitrophenyl *o*-nitrobenzenethiolsulfinate and *o*-nitrophenyl *o*-nitrobenzenethiolsulfonate. Since we could not obtain the thiolsulfinate, there is no way to estimate in what ratio these three compounds are mixed to make up Zincke's ortho compound.

A question still remains why the *o*-nitrothiolsulfinate does not disproportion so readily as compared to the *p*-isomer. We cannot offer

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[6] H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **73**, 129 (1954).

[7] L. D. Small, J. H. Bailey and C. J. Cavallito, *J. Am. Chem. Soc.*, **69**, 1710 (1947).

[8] H. Bredereck, A. Wagner, H. Beck and R.-J. Klein, *Ber.*, **93**, 2736 (1960).

* After this work was completed in our laboratory, we learned that Vinkler has also suggested the similar intermediate in their kinetic study of hydrolysis of various sulfenyl chlorides: E. Vinkler, *Acta Chim. Hung.*, **11**, 15 (1957); **22**, 345 (1960).

[9] C. J. Cavallito, La Verre and L. D. Small, *Chem. Abstr.*, **44**, 9977 (1950).

any satisfactory answer with our present knowledge. Probably the steric arrangement of ortho groups has some role in stabilizing the thiolsulfinate. In this connection, it is interesting to note that *o*-nitrobenzenesulfenyl methyl ether was easily obtained when *o*-nitrobenzenesulfenyl chloride was reacted with sodium methoxide[2] and is quite stable while the *p*-isomer could not be obtained in pure form. We could not reproduce the same result when we followed Zincke's procedure[1], or slightly modified ways. Everytime, we found that the product was mixed with *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate and *p, p'*-dinitrodiphenyl disulfide.

Experimental

So-called Zincke's *p*-nitrobenzenesulfenic anhydride was prepared by hydrolyzing the corresponding sulfenyl chloride[1]. Zincke reported this compound darkened at 126°C and melted with decomposition at 160°C. After repeated recrystallization from benzene, it lost the darkening point and melted with decomposition at 151∼153°C. Fractional crystallization was tried using benzene as solvent, always obtaining the same compound.

Found: C, 44.69; H, 2.63. Calcd. for $C_{12}H_8 \cdot N_2O_5S_2$: C, 44.44; H, 2.49%.

UV λ_{max} mμ (log ε): 270 (4.15), 303 (4.17).

IR characteristic band: 1145 cm^{-1} (s).

***o*-Nitrobenzenesulfenic anhydride** was also prepared in the same way[2]. The darkening point of this compound fluctuated around 70°C, melted at 181∼196°C (darkened at 92∼93°C., fused and did not melt until heated abov 180°C)[2].

Found: C, 44.31; H, 2.60%. Calcd. the same to *p*-isomes.

UV λ_{max} mμ (log ε): 234 (4.37), 326 (3.88).

IR characteristic band: 1108 (s), 1145 cm^{-1} (m).

***p*-Nitrophenyl *p*-nitrobenzenethiolsulfonate and ortho analog** were both prepared from the reaction of the silver salts of sulfinic acids and sulfenyl chlorides[1,2], m. p. 182∼183°C and 145∼145.5°C respectively.

UV spectrum for *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate: λ_{max} mμ (log ε): 262 (4.29), 290 (4.00) and IR characteristic band: 1145 cm^{-1} (s).

UV spectrum for ortho analog: λ_{max} mμ (log ε): 231 (4.30) and IR characteristic bands: 1360 (s), 1145 cm^{-1} (s).

***o*-Nitrobenzenesulfenyl methyl ether** was prepared from the reaction of *o*-nitrobenzenesulfenyl chloride and sodium methoxide[2], m. p. 51∼52°C.

***p*-Nitrobenzenesulfenyl methyl ether** was obtained following the procedure by Zincke[1]. The compound darkened at 125∼135°C and melted with decomposition around 151∼156°C. The reaction was also carried out in hexane as solvent, cooling with ice or shortening the reaction time always attaining the same result.

Found: C, 44.96; H, 2.64. Calcd. for $C_7H_7NO_3 \cdot S$: C, 45.40; H, 3.70%.

UV λ_{max} mμ (log ε): 270, 312 (3.99).

IR characteristic band: 1145 cm^{-1} (s).

Oxidation of *p, p'*-Dinitrodiphenyl Disulfide.—To 10 g. of *p, p'*-dinitrodiphenyl disulfide dissolved in 450 cc. of chloroform was added for 40 min. an equivalent amount of perbenzoic acid in chloroform with vigorous stirring and cooling in an ice-bath[6,7]. Stirring was continued to next day at room temperature. When the disulfide was completely dissolved, the solution was neutralized with sodium bicarbonate solution, washed with water and dried over sodium sulfate. Chloroform was evaporated at room temperature and the precipitate was collected fractionwise after separated off the starting material. The second crop was recrystallized from benzene. This crystals gradually got dark and melted at 148∼151°C with decomposition, giving 2 g. of pale yellow crystals.

Found (for the second crop): C, 44.94; H, 2.55. Calcd. for $C_{12}H_8N_2O_5S_2$: C, 44.44; H, 2.49%.

UV spectrum for the second crop; λ_{max} mμ (log ε): 271 (4.14), 305 (4.18).

IR characteristic band of the second crop: 1145 cm^{-1} (s).

IR characteristic bands of the third crop: 1145 cm^{-1} (s), 1118 cm^{-1} (s).

Oxidation of *o, o'*-Dinitrodiphenyl Disulfide.—*o, o'*-Dinitrodiphenyl disulfide was oxidized similarly with perbenzoic acid under irradiating with ultraviolet light[9], obtaining a small amount of product which darkened at about 100°C and decomposed at 128∼130°C. When recrystallized from petroleum ether-benzene mixture, white and yellow crystals formed. Both crystals were mechanically separated. The white crystals were recognized by infrared spectra to be corresponding to the thiolsulfonate and the yellow to the disulfide, respectively.

Identification of the Equimolar Mixture.—When an equimolar mixture of authentic *p*-nitrophenyl *p*-nitrobenzenethiolsulfonate and *p, p'*-dinitrodiphenyl disulfide was recrystallized from benzene, the resulting crystals melted at 152.5∼153.5°C. Ultraviolet and infrared spectra of the crystals coincided well with those of the corresponding alleged sulfenic anhydride I.

UV λ_{max} mμ (log ε): 270 (4.15), 302 (4.16).

IR characteristic band: 1145 cm^{-1} (s).

The crystals, recrystallized from an equimolar mixture of *o*-nitrophenyl *o*-nitrobenzenethiolsulfonate and *o, o'*-dinitrodiphenyl disulfide melted gradually from 136°C to 157°C with decomposition and had bands at 1360 and 1145 cm^{-1}, but had no band at 1108 cm^{-1}.

^{18}O Exchange Reactions.—Nitrobenzene, 0.7 g., was dissolved in 10 cc. of ^{18}O-enriched 98% sulfuric acid (0.5 atom % ^{18}O) at 0°C for 10 min., then was diluted with ice-water. The nitrobenzene recovered was distilled once, obtaining 0.5 g., and was subjected to ^{18}O analysis[10].

^{18}O for $C_6H_5NO_2$	0.209%
^{18}O for tank CO_2	0.210%

^{18}O Enriched Zincke's So-called *p*-nitrobenzenesulfenic anhydride was prepared from the hydrolysis of *p*-nitrobenzenesulfenyl chloride with equimolar amount of $H_2{}^{18}O$ (1.5 atom % ^{18}O) in glacial acetic acid.

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10) D. R. Christman and S. Oae, *Chem. & Ind.*, 1959, 1251.

TABLE II

Treatment	Darkening point	Melting point, °C	The ratio of intensity ($-\log T$) at 270 mμ and 303 mμ
Only washed with ether, quickly dried	~123°C	145~155	1 : 0.885
Heated at 72~73°C for 3 hr. in vacuo	Obscure	148~150	1 : 0.948
Heated at 72~73°C for 6 hr. in vacuo	Almost indistinct	149~151	1 : 1.032
Repeated recrystallization, well dried in vacuo	Did not occur	151~153	1 : 1.017

^{18}O for p,p'-$O_2NC_6H_4S^{18}OSC_6H_4NO_2$	0.46%
^{18}O for tank CO_2	0.210%

One gram of this compound was dissolved into 98% H_2SO_4 at 0°C, and was kept standing for 15 min., then filtered and the filtrate was poured into ice-water. The precipitate formed was collected, washed with a sufficient amount of water, repeatedly, dried, and recrystallized from benzene, m. p. 156~168°C, 0.25 g.

^{18}O for p,p'-$O_2NC_6H_4S^{18}OSC_6H_4NO_2$	0.44%
^{18}O for tank CO_2	0.210%

In the case of ortho compound, the starting material could not be recovered.

The Variation of Melting Point and Ultraviolet Spectrum of *p*-Nitrobenzene-sulfenic Anhydride only Washed with Ether. — Fresh *p*-nitrobenzenesulfenic anhydride only washed with ether and quickly dried was treated under various conditions, and melting points and the ultraviolet spectra taken with the corresponding changes are as shown in Table II.

Ultraviolet Spectra.—All spectra were taken on Shimadzu model RS-27 auto-recording spectrophotometer using the solutions of the compounds dissolved in purified dioxane.

Infrared Spectra. — In all spectrophotometries potassium bromide disks were used.

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