THE STEREOCHEMISTRY OF CHLORINATION
OF SULFOXIDES WITH NITROSYL CHLORIDE

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Stereochemistry of Chlorosulfoxides

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SUMMARY

The reaction of nitrosyl chloride, with sulfoxides in the presence of pyridine was investigated. The reaction has been shown to be stereospecific at the sulfur atom with retention of configuration at this asymmetric center.

Racemization of sulfoxides by nitrosyl chloride was seen. (+)-Chloromethyl phenyl sulfoxide was shown to be of the same configuration as (+)-methyl phenyl sulfoxide.

The kinetics of the reaction indicate that only two moles of nitrosyl chloride react with each mole of sulfoxide.

STATEMENT OF THE PROBLEM

Several methods have been found for the synthesis of α -chlorosulfoxides. All these reactions are characterized by the fact that one diastereomer or the other is preferentially produced. Chang and Loeppky¹ found that nitrosyl chloride in the presence of pyridine gave α -chlorination of sulfoxides as shown below:

It was the object of the present research to find the stereochemical course of the reaction and further define its mechanism.

HISTORICAL

1. Alpha-Chlorosulfoxides

In 1968 Loeppky and Chang¹ reported a new and general synthesis of α-chlorosulfoxides. Alkyl sulfoxides reacted with a nitrosyl chloride-pyridine mixture in chloroform to produce α-chlorosulfoxides in high yield. Previous to this work no general method for producing α-chlorosulfoxides had been reported although several individual cases had been reported.

The nitrosyl chloride method utilizes pyridine to trap hydrogen halides. Since then, several general methods of chlorinating sulfoxides have been found, all but one utilizing pyridine to trap hydrogen chloride and thus preventing Pummerer-Smythe hydrogen halide cleavage reactions²⁻⁴.

Hojo and Yoshida⁵ found that p-toluene sulfonyl chloride in the presence of pyridine, chlorinated methyl phenyl sulfoxide in 23% yield.

Cinquini, Colonna and Montanari reported that alkyl sulfoxides react with iodobenzene dichloride in pyridine at -40° to give α -chlorosulfoxides in 60-80% yield¹⁴. This was found as a result of studies with the oxidation of sulfides.

More recently, Iriuchijima and Tsuchihashi⁶ found that 2 moles of *t*-butyl hypochlorite react with one mole of alkyl sulfoxide, in the presence of pyridine, to produce α -chlorosulfoxides.

They also found that *t*-butyl hypochlorite chlorinated alkyl sulfoxides by a free radical mechanism in the presence of anhydrous potassium acetate at 0° in 3 to 4 hours in 45-50% yield.

These same workers have lately found that chlorine and sulfonyl chloride in the presence of pyridine reacts with 2-phenyl ethyl phenyl sulfoxide to give the corresponding 2-chlorosulfoxide in 92% yield⁷. It might be noted that the position alpha to the sulfinyl group is more susceptible to chlorination than the benzyl position.

Recently they have extended the reaction to elemental bromine in pyridine or N-bromosuccinimide/bromine in pyridine to give α-bromo sulfoxides²⁷.

II. Stereochemistry

The methylene hydrogens alpha to a sulfinyl group have shown a remarkable magnetic and chemical nonequivalence. This has been shown to be mainly due to conformational preference⁸⁻⁹. Rauk, Bunzel, Moir and Wolfe reported the kinetic and spectroscopic nonequivalence of the methylene hydrogens when benzyl methyl sulfoxide underwent base catalyzed exchange in 1M NaOD-D₂O¹⁰. They reported in

this paper and in subsequent ones¹¹⁻¹² that the S-configuration is obtained. Baldwin, Hackler and Scott¹³ later found this to be in error, with the R-configuration the correct one.

Cinquini, Colonna, and Montanari found that α -chlorination of sulfoxides by iodobenzene dichloride involves the proton diastereotopic to that which is preferentially exchanged by deuterium in NaOD-D₂O¹⁴.

Iriuchijima and Tsuchihashi realizing the stereospecificity of all the α -chlorination reactions of sulfoxides, identified the diastereomeric α -chlorobenzyl phenyl sulfoxides made from benzyl phenyl sulfoxide.

SS - RR

SR - RS

They concluded, by means of solvent induced chemical shifts, that **I** is the major diastereomer produced from all the ionic chlorinating agents (See Table I) and that **II** the major one from free radical chlorination by t-butyl hypochlorite-potassium acetate method⁶.

TABLE I

Ratio of diastereomers from Chlorination of Sulfoxides

Method of chlorination	Ratio of diastereomers (I/II)
NOCl/pyridine	90:10
<u>p</u> -toluenesulfonyl chloride	85:15
Iodobenzene dichloride	95:5
(CH ₃) ₃ COCl/pyridine	75:25
(CH ₃) ₃ COCl	30:70

RESULTS AND DISCUSSION

Since the reaction of nitrosyl chloride with sulfoxides in the presence of pyridine produces such diastereomerically pure material, it was of interest to see if the sulfur atom undergoes retention or inversion of configuration and if the prochiral center at carbon undergoes retention or inversion during the course of the reaction.

It was decided to attack each asymmetric center individually since the sulfoxide pyramid has been shown to maintain its configurational stability under a variety of conditions¹⁶. The synthesis of an optically active sulfoxide is best done by the method of Anderson¹⁵, which was later improved on by Mislow¹⁶⁻¹⁷. Methyl phenyl sulfoxide was to be made as it would give an α -chloro sulfoxide without an asymmetric center at the α -carbon and thus not give rise to a mixture of diastereomers.

Methanesulfinyl chloride was prepared according to the method of Douglas and Farah¹⁸ from the reaction of methyl disulfide with chlorine in glacial acetic acid at -10° .

The methanesulfinyl chloride was then allowed to react with (-)-menthol to produce (-)-menthyl methanesulfinate

The sulfinate ester was then reacted with phenyl magnesium bromide at -20° to give optically active (+) methyl phenyl sulfoxide in approximately 30% optical purity¹⁵. Mislow has found that this gives the R-configuration¹⁹.

The optically active sulfoxide was then reacted with nitrosyl chloride and pyridine to give the corresponding α -chlorosulfoxide. When the reaction was run overnight at room temperature, it gave racemic chloromethyl phenyl sulfoxide.

It was thought that the reaction was run too long and so it was run again and quenched at about 50% of the reaction as determined by nmr. This time it was found that it gave (+)-chloromethyl phenyl sulfoxide and partially racemized unreacted (+)-methyl phenyl sulfoxide.

The partial racemization of sulfoxides is probably due to the nitrosyl ion or oxides of nitrogen. Nitrogen tetroxide produces racemization and O^{18} exchange of the sulfoxides at the same rate²⁰⁻²¹. Kunieda, Sakai and Oae²¹ suggested that the following was the mechanism for the racemization:

It seems likely that nitrosyl chloride acts in a similar manner.

Since the starting material is partially racemized, it is not certain whether the chloromethyl phenyl sulfoxide is susceptible to racemization by the nitrosyl ion although it seems probable. No attempt was made to determine the rate of racemization of either the original sulfoxide or the α -chloro sulfoxide.

In order to find if the reaction proceeded with retention or inversion of configuration at sulfur, the configuration at sulfur of the chloromethyl phenyl sulfoxide was needed. It was decided to reduce this compound back to the original sulfoxide and measure its rotation. Low pressure hydrogenation with palladium on carbon as a catalyst was found to be a suitable reducing agent with α -chlorobenzyl benzyl sulfoxide. Pyridine was added to take up hydrogen chloride and thus prevent cleavage and racemization reactions.

When this reaction was applied to the optically active chloromethyl phenyl sulfoxide, a positive rotating methyl phenyl sulfoxide was obtained showing retention of configuration at sulfur in the α -chlorination reaction.

It will be shown later that some base catalyzed exchange of the α -hydrogens does occur. It has been found that mild base catalyzed exchange does not racemize the sulfur asymmetric center. Cram and Pine²³ found that potassium *t*-butoxide does not racemize sulfoxides. Later, Jacobus and Mislow²⁴ found that methyl lithium does racemize and cleave sulfoxides.

In order to find out if the α -chlorination reaction proceeds with inversion or retention of configuration at the α -carbon, it was decided to use a sequence of reactions involving the known configuration of α -chlorobenzyl phenyl sulfoxide. It was thought that if the chlorine could be stereospecifically replaced by deuterium, the product would be diastereomerically pure of known configuration.

Considering the reduction to go with retention of configuration, the deuterated diastereomer could be reacted with nitrosyl chloride-pyridine to produce α -chlorobenzyl phenyl sulfoxide if the transformation at the α -carbon undergoes retention of configuration, and α -chlorodeuterio benzyl phenyl sulfoxide if inversion.

SCHEME #1

After several trials, this scheme was found to be inoperable because the pyridine in the deuteration step causes base catalyzed exchange of the α -hydrogens during the long period required for the hydrogenation. This sequence of reactions may still offer a method of determining the reaction stereochemistry at the α -carbon if a suitable stereospecific method of reducing the chlorine is found. There is not a sufficient difference in the rates of exchange of the two methylene hydrogens of the similar system of benzyl p-chlorophenyl sulfoxide, to allow direct synthesis of a stereospecifically deuterated benzyl phenyl sulfoxide²².

Some cursory kinetic work was done by nmr to determine the order of each reactant in the nitrosyl chloride-pyridine reaction. The absorption due to the benzylic protons in benzyl phenyl sulfoxide was monitored as a function of time. Benzyl phenyl sulfoxide was chosen as the chemical shift of its benzylic hydrogens are clearly separated from the single benzyl hydrogen resonance of the α -chlorobenzyl phenyl sulfoxide produced. Four kinetic runs are shown in appendix I. Each of the reactant concentrations were varied while holding the others constant. Using run one as a standard, run two decreases the sulfoxide concentration, run three increases the nitrosyl

chloride concentration, and run four increases the pyridine concentration. When the sulfoxide concentration was increased, the rate of the reaction was increased. The reaction appears to be approximately first order in sulfoxide.

When the nitrosyl chloride concentration was increased, the rate increased and also appears to be first order. No rate change was seen when the pyridine concentration was varied. The most striking thing about the data is that in no case did the reaction go to completion. This is why the order of sulfoxide and nitrosyl chloride could not be exactly determined from the Noyes equation²⁸ correlating half life and concentration with order of a reactant. Although the rate was not affected by pyridine, the percent of conversion of sulfoxide to α -chlorosulfoxide decreases as the pyridine concentration was increased.

The kinetic data were tested with integrated rate equations. The equations were developed with the assumption that the stoichiometry has only two moles of nitrosyl chloride reacting with one mole of sulfoxide and not with three to one as Chang²⁶ had earlier thought.

This is reasonable primarily because the redox stoichiometry demands it, and secondly, because the reaction was observed to go beyond two thirds completion when the ratio of nitrosyl chloride to sulfoxide was two to one. When the reaction is assumed to be first order in sulfoxide and nitrosyl chloride, a plot of the integrated rate function versus time is linear over two thirds of the reaction, but then falls away (See Plot /). Other integrated rate functions did not fit the data at all. When one takes into account the facts that the reaction does not go to completion, the pyridine effect on yield, and the integrated rate equation not fitting the data in the last third of the reaction, all indicate an inhibiting reaction whose effect on the rate is only felt near the end of the reaction. Pyridine may well be involved in this. Time did not allow a more definitive study, but determination of the reaction mechanism would involve more kinetics and this would more than likely mean a need to follow nitrosyl ion concentration as a function of time.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer model 237-B spectrophotometer. Nuclear magnetic resonance spectra (nmr) were run on a Varian A-60 Spectrophotometer using tetramethylsilane as an internal standard.

Kinetics were also run on a Varian A-60 Spectrophotometer using the methyl group on p-chloro toluene as an internal standard. The kinetics were done as follows: a standard solution of double recrystallized benzyl phenyl sulfoxide, purified pyridine (washed, doubly distilled over calcium hydride and stored over molecular sieve type 4A), distilled p-chloro toluene and purified chloroform (washed with 20% sulfuric acid, water, and distilled over anhydrous calcium chloride). Nitrosyl chloride was condensed in a tared volumetric and weighed while still frozen. A portion of the standard solution was added and then mixed while bringing up the total volume with chloroform. After thorough mixing, a portion was placed in a nmr spin tube and the reaction followed at constant temperature (40°) by means of integration of the benzylic proton signal of benzyl phenyl sulfoxide, and of the internal standard as a function of time.

Optical rotations were observed on a D. C. Rudolph and Sons polarimeter Model 121, accurate to 0.002° at the sodium D wavelength. The melting and boiling points are uncorrected.

l-menthol, dibenzyl sulfoxide, methyl disulfide, benzyl phenyl sulfide, and methyl phenyl sulfide were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wis., U.S.A.

The Synthesis of Benzyl Phenyl Sulfoxide

Hydrogen peroxide (53 ml, 30%, 0.49 mole) was added to a solution of 100 g (0.5 mole) benzyl phenyl sulfide in 500 ml acetone. The mixture was stirred for two days after which the solution was alternately cooled and filtered giving 90 g (87%) crude product. This was then recrystallized from absolute ethanol giving 85 g (83%) pure benzyl phenyl sulfoxide: mp $122.5\text{--}123^\circ$ (lit.²⁵ $122\text{--}123^\circ$); ir (nujol) 1025 and 1040 (SO); nmr (CDCl_3) δ 3.90 (s, 2, $\text{CH}_2\text{--C}_6\text{H}_5$), δ 6.90–7.70 (m, 10, $\text{C}_6\text{H}_5\text{CH}_2\text{SOC}_6\text{H}_5$).

The Synthesis of α -Chlorobenzyl Phenyl Sulfoxide

Benzylphenyl sulfoxide (20 g, 0.093 mole) and pyridine (23.7 g, 0.3 mole) was dissolved in 150 ml of chloroform in a 300 ml round bottom flask with magnetic stirrer. The solution was cooled to -50° and nitrosyl chloride (19.65 g, 0.3 mole)

was added in one portion with rapid stirring. The reaction mixture was brought to room temperature and after four hours showed complete reaction by nmr. The mixture was then shaken with 300 ml sulfuric acid (40%) and then the chloroform layer separated. The aqueous layer was then washed three times with 50 ml of chloroform and the combined chloroform solutions dried over anhydrous magnesium sulfate with a couple drops of pyridine to retard decomposition. The chloroform was then stripped on a rotary evaporator. The product was then double recrystallized from absolute ethanol to give 16 g (70%) white crystals: mp 122.5-123° (lit.²⁶ 122.5-123°); ir (nujol) 1050 and 1095 cm^{-1} (SO) (lit.²⁶ 1050, 1095 cm^{-1}); nmr (CDCl_3) δ 5.50 (s, 1, SO CHClC_6H_5) (lit.²⁶ 5.59), δ 6.95-7.58 (m, 10, C_6H_5) (lit.²⁶ 7.02-7.60).

The Synthesis of Benzyl α -Chlorobenzyl Sulfoxide

A 200 ml round bottom flask was filled with a solution of 23 g (0.10 mole) of dibenzyl sulfoxide and 23.7 g (0.30 mole) of pyridine in 125 ml of chloroform. Nitrosyl chloride (19.7 g, 0.30 mole) was condensed into a tared flask and added in one portion to the above stirred solution at -10° . The mixture was stirred overnight at room temperature whereupon 200 ml of 40% sulfuric acid was added and stirred for 15

minutes. The chloroform layer was separated and the aqueous layer extracted with two 50 ml portions of chloroform. The combined chloroform solutions were then stripped of solvent on a rotary evaporator and the product recrystallized from absolute ethanol to give 20 g (75%) of benzyl alpha-chloro benzyl sulfoxide: mp 112-113° (lit.²⁶ 118-118.5°); nmr (CDCl₃) δ 3.89, 4.00 (d of d, 2, C₆H₅CH₂SO), 5.50 (s, 1, C₆H₅CHClSO), 7.40 (s, 5, C₆H₅CH₂SO), 7.48 (s, 5, C₆H₅CHClSO).

Reduction of Benzyl α -Chlorobenzyl Sulfoxide

To a solution of 5.3 g (0.02 moles) of benzyl α -chlorobenzyl sulfoxide, and 3 g (0.03 moles) pyridine in 150 ml absolute ethanol, palladium on carbon catalyst (1.65 g, 5%) was added and the mixture placed in a low pressure hydrogen shaker. The system was repeatedly evacuated and flushed with hydrogen and then shaken for 18 hours at 33 psi. The reaction mixture was then filtered and stripped on a rotary evaporator. The oil was then taken up in pet ether C-benzene and washed with water. The product (1.51 g, 0.0061 mole) was then fractionally recrystallized out of the solution the first fraction being almost pure dibenzyl sulfoxide: mp 132-134° (lit.²⁵ 132-134°); ir and nmr spectra were identical with a known sample.

The Synthesis of Methanesulfinyl Chloride

A solution of methyl disulfide (94.2 g, 1 mole) in in glacial acetic acid (120 g, 2 moles) was placed in a 1 liter three neck flask equipped with an efficient sealed stirrer, gas inlet tube extending within one inch of the reaction mixture, and a gas outlet tube leading to a hydrogen chloride trap. The flask was cooled to -10 to -15° throughout the reaction. Chlorine (212.7 g, 3 moles) was condensed in a tared flask and then absorbed by the reaction mixture. The flask was then warmed to 35° with vigorous evolution of hydrogen chloride. The reaction mixture was fractionally distilled on a 10 cm glass helices packed column giving 158 g (81%) methane sulfinyl chloride: bp $55-58^{\circ}$ (40mm) [lit.¹⁸ $55-59^{\circ}$ (40mm)]; nmr (CCl_4) δ 3.59 (s, 3, CH_3S (O) Cl) ; Ir (neat) 1140 (SO).

The Synthesis of (-)-Menthyl Methanesulfinate

A solution of (-)-menthol (78.1 g, 0.500 mole) and pyridine (40.3 g, 0.510 mole) in ether (50 ml) was added to a three neck flask equipped with a mechanical stirrer and dropping funnel. The mixture was cooled to 0° with an ice bath and a solution of methanesulfinyl chloride (50.2 g, 0.510 mole) in anhydrous ether (150 ml) was added

dropwise with stirring. After the addition was complete, the mixture was stirred overnight in the ice bath and then extracted with cold water, cold 10% hydrochloric acid, cold aqueous sodium bicarbonate and again with cold water, in that order. After drying over sodium sulfate and subsequent removal of the ether on a rotary evaporator, the oily product was fractionally distilled on a 20 cm glass helices packed column and gave 94 g (90%) of pure (-)-Menthyl Methanesulfinate: bp 68-72° (0.05 mm) [lit.¹⁵ 88-89° (0.4 mm)] ; $[\alpha]_D^{25}$ -99° (C 4.31, acetone) [lit.¹⁵ $[\alpha]_D^{25}$ -99° (C 2.04, acetone)] ; nmr (CDCl₃) δ 7.40 (s, 3, CH₃S (O) C₆H₅), ir (neat) 1137 cm⁻¹ (SO).

The Synthesis of (+)-Methyl Phenyl Sulfoxide

A phenyl magnesium bromide Grignard reagent was prepared from bromobenzene (31.4 g, 0.200 mole) and magnesium (5.5 g, 0.23 g -atom) in anhydrous ether (100 ml). This was added dropwise over forty minutes to a stirred solution of (-)-menthyl methane sulfinate 38 g, 0.17 mole, $[\alpha]_D^{25}$ -99° (C 4.31, acetone) in ether (100 ml). The temperature throughout the reaction kept at -15 to -20°. The reaction was warmed to 25°, stirred for 10 minutes, and then hydrolyzed with saturated ammonium chloride (200 ml). The organic layer

was dried over magnesium sulfate, filtered and concentrated on a rotary evaporator to give an oil which was then fractionally distilled on a 20 cm glass helices packed column to give 12 g (47%) methyl phenyl sulfoxide: bp 104° (0.75 mm) [lit.¹⁵ 85° (0.5 mm)] ; $[\alpha]_D^{25} +60^\circ$ (C 2.28, acetone) [lit.¹⁵ $[\alpha]_D^{25} +23$ (C 2.29, acetone)] ; nmr (CHCl₃) δ 2.68 (s, 3, CH₃-S (O) C₆H₅), δ 7.52 (m, 5, CH₃S (O) C₆H₅).

Reaction of (+)-Methyl Phenyl Sulfoxide with Pyridine and Nitrosyl Chloride

A solution of optically active methyl phenyl sulfoxide (5 g, 0.0357 mole, $[\alpha]_D^{25} +60^\circ$) and pyridine (12.3 g, 0.12 mole) in 50 ml chloroform was cooled to -20°. A flask was tared and 7.86 g (0.12 mole) of nitrosyl chloride was condensed in it and then added in one portion to the above solution. The reaction was followed by nmr until 50% reaction had occurred. The reaction was then quenched with 100 ml of 40% sulfuric acid in water. The chloroform layer was then separated, and the aqueous layer washed with chloroform and the combined organic layers stripped of chloroform on a rotary separator. The oily product was then separated by means of thin layer chromatography on silica gel with chloroform eluent. This afforded methyl phenyl sulfoxide $[\alpha]_D^{25} +17^\circ$ (C 2.29, acetone); $R_f = 0.3$ nmr (CDCl₃) δ 2.70 (s, 3, CH₃-S (O) C₆H₅) 7.58 (m, 5, C₆H₅S(O)CH₃),

and chloromethyl phenyl sulfoxide $[\alpha]_D^{25} +21.8^\circ$ (C 2.23, acetone) ; $R_f = 0.6$; nmr (CDCl_3) δ 4.78, 4.82 (dof d, 2, CH_2ClSO) (lit.²⁶ δ 4.39, 4.62), 7.88-8.28 (m, 5, C_6H_5) (lit.²⁶ 7.48-7.88). The products were shown to be free of impurities by nmr and tlc.

Reduction of (+)-Chloromethyl Phenyl Sulfoxide

A low pressure hydrogenation apparatus (Parr type) was charged with 0.3 g (0.0017 mole) of chloromethyl phenyl sulfoxide, 10 ml of pyridine, and palladium on carbon (5%) catalyst (0.03 g) in 50 ml of absolute ethanol. The pressure was raised to 45 psi and sample shaken for three days. The product was purified by preparative thin layer chromatography on silica gel with chloroform eluent. The silica gel of the band containing methyl phenyl sulfoxide was extracted repeatedly with methanol and then acetone. The product was filtered and stripped of solvent giving a clear oil shown to be methyl phenyl sulfoxide and free from impurities by thin layer chromatography and nmr: $[\alpha]_D^{25} + 14^\circ$ (C 1.19, acetone); nmr (CDCl_3) δ 2.63 (s, 3, CH_3S (O) C_6H_5), (lit.²⁶ 2.68) δ 7.40-7.80 (m, 5, C_6H_5).

Reduction of α -Chlorobenzyl Phenyl Sulfoxide with Deuterium

Diastereomerically pure (SS, RR) α -chlorobenzyl phenyl sulfoxide (4.2 g, 0.194 mole) was placed in a slurry of 0.42 g palladium on charcoal (5%) and 5 g pyridine in 100 ml absolute ethanol. This was put in a low pressure hydrogenation apparatus (Parr type) and allowed to react for three days with deuterium at 19 psi. The solution was filtered and stripped and fractionally recrystallized from an ethanol-water mixture to give 1 g benzyl phenyl sulfoxide identical to the known material and showing no deuterium according to nmr integration.

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APPENDIX I

Derivation of Kinetic Equations

Considering the stoichiometry of the reaction to be:

let:

SO_t = sulfoxide concentration at any time t

SO_i = initial sulfoxide concentration

NO_t = nitrosyl chloride concentration at any time t

NO_i = initial nitrosyl chloride concentration

If the nitrosyl chloride reacted as half of the sulfoxide reacted at any time, then:

$$\text{NO reacted} = \frac{\text{SO}_i - \text{SO}_t}{2}$$

$$\text{NO}_t = \text{NO}_i - \frac{(\text{SO}_i - \text{SO}_t)}{2}$$

If the rate is first order in SO and NO then:

$$\frac{-d\text{SO}}{dt} = k [\text{NO}_t] [\text{SO}_t]$$

$$\frac{-d\text{SO}}{dt} = k_2 \left[\text{NOCl}_i - \frac{(\text{SO}_i - \text{SO}_t)}{2} \right] [\text{SO}_t]$$

Integration gives:

$$kt = \frac{2}{2NO_1 - SO_1} \left[\ln \left(\frac{2NO_1}{SO_1} \right) \left(\frac{SO_+}{2NO_1 - SO_1 + SO_+} \right) \right]$$

Plotting of the data of three runs gives:

$$k = 0.0070 \pm .0004$$

$$k = 0.0100 \pm .0006 \text{ and}$$

$$k = 0.0068 \pm .0005$$

If the rate is first in SO and second order in NO then:

$$\frac{-dSO}{dt} = k [NO]^2 [SO]$$

$$\frac{-dSO}{dt} = k \left[NO_1 - \frac{(SO_1 - SO_+)}{2} \right]^2 [SO_+]$$

Integration gives:

$$kt = \left[\frac{1}{A(A + 1/2 SO_1)} - \frac{1}{A^2} \ln \frac{A + 1/2 SO_1}{SO_1} \right] - \left[\frac{1}{A(A + 1/2 SO_+)} - \frac{1}{A^2} \ln \frac{A + 1/2 SO_+}{SO_+} \right]$$

$$\text{where } A = NO_1 - 1/2 SO_1$$

Plotting of the data of three runs gives:

$$k = 0.0036 \pm 0.0002$$

$$k = 0.0091 \pm 0.0005$$

$$k = 0.0061 \pm 0.0004$$

PLOT #1

PLOT #2

PLOT #3

PLOT #4

Integrated Rate Function for

34

$$-\frac{dSO}{dt} = k [SO] [NO]$$

$$-\frac{dSO}{dt} = k [SO] [NO]$$

Integrated Rate Function for

$$-\frac{dSO}{dt} = k [SO] [NO]$$

Integrated Rate Function for

$$-\frac{dSO}{dt} = k [SO] [NO]^2$$

$$-\frac{dSO}{dt} = k [SO] [NO]^2$$

$$-\frac{dSO}{dt} = k [SO] [NO]^2$$

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Source information

Identifier	Microfilm reel# T210-215
Format	Microfilm
Content type	Text
Notes	

Capture information

Date captured	2018
Scanner manufacturer/model	ScanPro 3000 /e-ImageData
Scanning software	PowerScan 3000(TM) v5.341
Optical resolution	600 dpi
Compression	LZW
Color settings	bitonal
File types	tiff
Notes	Scanned from microfilm; no editing done.

Derivatives - Access copy

Editing software	Photoshop
Resolution	600 dpi
Color	grayscale
File types	pdf
Notes	Converted from tiff to pdf using Adobe Acrobat Pro DC.