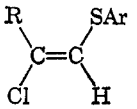
Reactions of Sulfenyl Chlorides and Their Derivatives. II.[1] The Kinetics, Orientation, and Stereochemistry of Addition of 2,4-Dinitrobenzenesulfenyl Chloride to 1-Phenylpropyne

George H. Schmid and Marvi Heinola[2]

Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada. *Received December 14, 1967*

Abstract: The reaction of 2,4-dinitrobenzenesulfenyl chloride with 1-phenylpropyne in chloroform at 50.98° follows a second-order rate law, first order in both reactants, and gives the Markovnikov-like product 1-phenyl-*trans*-1-chloro-2-(2,4-dinitrophenylthio)propene (**3**) and the anti-Markovnikov-like product 1-phenyl-*trans*-2-chloro-1-(2,4-dinitrophenylthio)propene (**5**) in 94 and 6% yields, respectively. A mechanism involving a cyclic sulfonium ion is suggested to account for the results.

While the electrophilic addition of sulfenyl chlorides to olefins has been extensively studied,[3] very little is known about the analogous addition to acetylenes. Kharasch and Assony[4] established that the reaction of 2,4-dinitrobenzenesulfenyl chloride with symmetrical acetylenes in acetic acid forms a 1:1 adduct as product. In the reaction with phenylacetylene in acetic acid it was found[5] that the reaction follows a second-order rate law, first order in each reactant, to form 2-chloro-2-phenylvinyl 2′,4′-dinitrophenyl sulfide as product. This result has recently been questioned by Modena and coworkers[6] who have found that in general the product of the addition of sulfenyl halides to terminal acetylenes is a mixture of two compounds, one having the Markovnikov-like orientation **1** and the other the anti-Markovnikov-like orientation **2**. The relative amounts of **1** and **2** seems to depend upon the nature of the acetylene,



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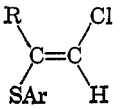

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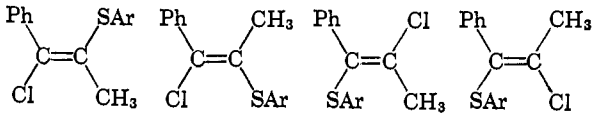
the sulfenyl chloride, and the solvent. Modena and coworkers[7] also report that the kinetics of the addition in aprotic solvents follow a second-order rate law.

The stereochemistry of these acetylene–sulfenyl chloride adducts, although assumed to be *trans*, has been established in only a few cases. Truce[8] showed that the adduct of *p*-toluenesulfenyl chloride with acetylene has the *trans* configuration and Montanari[9] established the *trans* configuration for the product formed by the addition of benzenesulfenyl chloride to chloroacetylene.

In order to provide further information concerning the reaction of sulfenyl halides with acetylenes, we report here a study of the kinetics, orientation, and stereochemistry of the addition of 2,4-dinitrobenzenesulfenyl chloride to 1-phenylpropyne.

Results

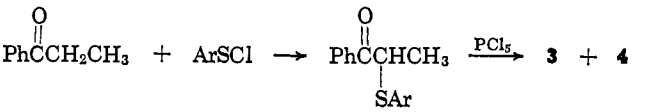
The four possible addition products 1-phenyl-*trans*- (**3**) and 1-phenyl-*cis*-1-chloro-2-(2,4-dinitrophenylthio)propene (**4**) along with 1-phenyl-*trans*- (**5**) and 1-phenyl-*cis*-2-chloro-1-(2,4-dinitrophenylthio)propene (**6**) were synthesized to provide authentic samples for comparison. Compounds **3** and **4** were prepared by



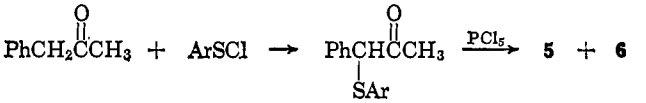
3 **4** **5** **6**

Ar = 2,4-dinitrophenyl

the method of Kharasch[5] starting with propiophenone.



Compound **3** was the major product from this reaction and in order to increase the amount of **4**, the product was subjected to uv irradiation. Separation of **3** and **4** was accomplished by chromatography on a 2% $AgNO_3$, silica column. Compounds **5** and **6** were prepared by a similar method starting with phenylacetone;



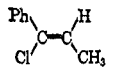
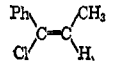
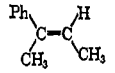
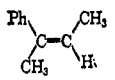
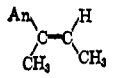
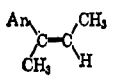
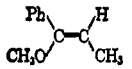
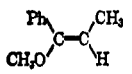
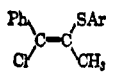
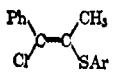
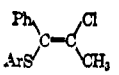
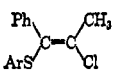
the sulfenyl chloride added to the more stable enol with the double bond conjugated with the phenyl group.

The geometry of the olefins **3**, **4**, **5**, and **6** was established by the differences in their nmr spectra. It has been found[10,11] that in derivatives of 1-phenylpropene the phenyl ring deshields the *β-cis* olefinic proton relative to a *trans* proton. Structural assignments have been based on this characteristic feature of 1-phenylpropene derivatives.[12,13] In addition to this effect, the

(1) Part I: G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).
(2) Holder of a National Research Council of Canada Studentship.
(3) N. Kharasch in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., London, 1961, Chapter 32.
(4) N. Kharasch and S. J. Assony, *J. Am. Chem. Soc.*, **75**, 1081 1953).
(5) N. Kharasch and C. N. Yiannios, *J. Org. Chem.*, **29**, 1190 (1964).
(6) V. Calò, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Letters*, 4399 (1965).
(7) L. Di Nunno, G. Melloni, G. Modena, and G. Scorrano, *ibid.*, 4405 (1965).
(8) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).
(9) F. Montanari and A. Negrini, *Gazzetta*, **87**, 1061 (1957).
(10) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).
(11) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).
(12) M. Barbieux, W. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belges*, **73**, 716 (1964).
(13) R. C. Fahey and C. S. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).

phenyl ring of an α-substituted 1-phenylpropene influences the chemical shift of the protons of a β-methyl group. Thus the protons of a β methyl group *cis* to phenyl are shielded relative to a *trans* methyl group. A few examples are listed in Table I. Others can be found in ref 12. On the basis of this correlation, it is possible to assign the structures shown to compounds **3**, **4**, **5**, and **6**.

Table I. Nmr Positions of the β-Methyl Groups in *cis*- and *trans*-β-Methylstyrene Derivatives[a]

	C_β–H	C_β–CH_3	Ref
	6.09	1.91	13
	5.95	1.70	13
	5.64	1.78	12
	5.50	1.56	12
	5.69	1.75	12
	5.45	1.57	12
	5.22	1.75	13
	4.67	1.65	13
	...	2.35	This work
	...	2.15	This work
	...	2.67	This work
	...	2.42	This work

[a] An = anisyl; Ar = 2,4-dinitrophenyl.

The product composition of the reaction of 2,4-dinitrobenzenesulfenyl chloride with 1-phenylpropyne was studied in chloroform at 50.98°. The products were isolated by evaporating the reaction mixture to dryness, and the solid was chromatographed on an alumina column to remove any starting material and disulfide. The solid was reisolated by evaporation to dryness and its nmr was taken in deuteriochloroform. The products were identified by a comparison of the positions of their methyl peaks in the nmr with those of the olefins **3**–**6** prepared by independent synthesis. Using this method, the products were found to be 94% **3** and 6% **5**. Control experiments with a mixture of known composition of compounds **3**–**6** established that the products are stable to the reaction conditions and no product fractionation occurs on chromatography. No difference in product composition was observed when the reaction was carried out in the presence of added oxygen or in the presence or absence of light. Since **3** is present in such large excess, there exists the possibility that its methyl peak at 2.35 ppm might obscure the methyl peak of a small amount of **6** at 2.42 ppm. By measuring the nmr of mixtures of known composition of **3** and **6**, it was found that, at compositions less than 4%, **6** does not appear distinctly in the nmr. Hence the product composition contains no more than 4% of the *cis* olefin **6**.

The rate of addition of 2,4-dinitrobenzenesulfenyl chloride to 1-phenylpropyne was determined in chloroform at 50.98°. The reaction was followed by observing the disappearance of the methyl peak of 1-phenylpropyne in the nmr spectrum of the reaction mixture. The reaction was followed for three half-lives. The kinetic data were found to fit a second-order rate equation, first order in each reactant, in accord with the findings of Kharash[5] and Modena and coworkers.[7] The rate constants, calculated from the integrated form of the usual second-order rate equation,[14] are collected in Table II.

Table II. Second-Order Rate Constants for the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to 1-Phenylpropyne in Chloroform at 50.98°

$[PhC{\equiv}CCH_3]$, M	[ArSCl], M	10^4k_2, M^{-1} sec^{-1}
0.1500	0.1500	1.2 ± 0.2
0.1810	0.1810	1.1 ± 0.2
0.1810	0.0905	1.1 ± 0.2
0.1406	0.1423	1.2 ± 0.2
0.1373	0.1445	1.2 ± 0.2
0.1296	0.1785	1.3 ± 0.2

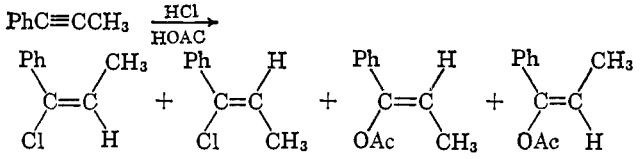
Discussion

Previous work by Kharasch and Assony[4] has established that the sulfenyl chloride is an electrophile in the reaction of 2,4-dinitrobenzenesulfenyl chloride with acetylenes. It is informative to compare the work reported here with other known electrophilic additions to acetylenes. The major studies in this field have been concerned with the additions of acids to acetylenes.

The evidence regarding the kinetics and stereochemistry of the addition of acids to acetylenes provides a fragmentary and rather confusing picture of the mechanism of this reaction. The addition of deuterium halide to propyne catalyzed by mercuric salts has been reported to be a stereospecific *trans* process.[15] On the other hand, Peterson[16] has found that trifluoroacetic acid adds nonstereospecifically to 3-hexyne, presumably *via* a vinyl cation intermediate, to give *cis*- and *trans*-3-hexen-3-yl trifluoroacetate. Fahey[17] has found that the addition of hydrogen chloride to 1-phenylpropyne in acetic acid follows a third-order rate law, first order in acetylene and second order in hydrogen chloride, to give 1-chloro-*cis*- and 1-chloro-*trans*-1-phenylpropene and

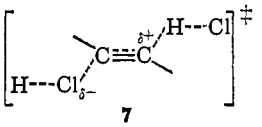
(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 15.
(15) H. Hunziker, R. Meyer, and G. Gunthard, *Helv. Chim. Acta*, **49**, 497 (1966).
(16) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966).
(17) R. C. Fahey and D. J. Lee, *ibid.*, **88**, 5555 (1966).

1-acetoxy-*cis*- and 1-acetoxy-*trans*-1-phenylpropene as primary products. These results have been interpreted



in terms of vinyl cation–hydrogen dichloride ion pairs as intermediates.

In contrast to this nonstereospecific addition, Fahey[18] has found that hydrogen chloride adds to 3-hexyne in acetic acid stereospecifically *trans*. To account for this result Fahey has postulated that *trans* addition occurs *via* transition state **7** in which the C–H and C–Cl bonds are simultaneously formed.



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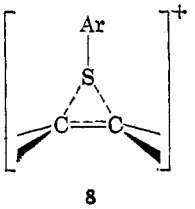
Neither the simultaneous nor the vinyl cation mechanism seems capable of explaining the results of the electrophilic addition of 2,4-dinitrobenzenesulfenyl chloride to 1-phenylpropyne. A simultaneous mechanism requires a rate law second order in electrophile while a vinyl cation mechanism would result in nonstereospecific addition. In addition neither mechanism predicts products with an anti-Markovnikov-like orientation.

The reactions of sulfenyl chlorides with olefins and acetylenes have several characteristics in common. Both follow a second-order rate law in fairly polar solvents, give exclusively *trans* addition products, and give both Markovnikov and anti-Markovnikov addition products.[19] These results for the addition of sulfenyl chlorides to olefins are consistent with a mechanism involving the cyclic sulfonium ion intermediate **8**.



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The results of this investigation imply that a cyclic sulfonium ion may also be an intermediate in the product-determining step of the addition of sulfenyl halides to acetylenes. Attack by the chloride ion in the product-determining step at both carbon atoms of the cyclic intermediate would account for the Markovnikov and anti-Markovnikov-like products. On the basis of the high Markovnikov-like/anti-Markovnikov-like product ratio (15:1) it would appear that the cyclic intermediate is highly unsymmetrical. The data available at the present time do not permit a more detailed picture of this intermediate. However it does appear as if the mechanisms of the addition of sulfenyl chlorides to acetylenes and olefins are very similar.

(18) R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, **89**, 2780 (1967).
(19) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **32**, 2925 (1967), and references cited therein.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Associates A-60 spectrometer. Samples were measured as approximately 10% w/v solutions in deuteriochloroform and chemical shifts are reported in parts per million (ppm) downfield from TMS as internal standard. Ultraviolet spectra were recorded on a Perkin-Elmer 350 spectrophotometer. A 450-W, Hanovia Type L, medium-pressure mercury arc lamp in an NA quartz-immersion cooling jacket was used for irradiation. Microanalysis was carried out by A. B. Gygli Microanalysis Laboratory, Toronto, Ontario.

1-Phenylpropyne. This compound was prepared according to the method of Hurd and Tockman[20] in 36% yield. The acetylene was purified by distillation, bp 84–87° (21 mm) (lit.[20] bp 90° (20 mm)), until a satisfactory nmr spectrum was obtained.

2,4-Dinitrobenzenesulfenyl Chloride. This compound was prepared according to the method of Lawson and Kharasch[21] and purified by recrystallization from carbon tetrachloride, mp 96–97° (lit.[21] mp 97–98°).

Chloroform was cleaned by washing commercial grade solvent with concentrated sulfuric acid and then with water. The solvent was dried over anhydrous $MgSO_4$ and then distilled, bp 61°.

2-(2,4-Dinitrophenylthio)propiophenone. This compound was prepared following the procedure of Kharasch.[5] The crude product was recrystallized from glacial acetic acid, yielding 18.1 g of amber crystals, mp 148–151°, yield 69%. An analytical sample was prepared by recrystallizing from methanol, mp 149–151°; $\gamma_{C=O}^{KBr}$ 1681 cm^{-1}; nmr 1.78 (3 H, doublet due to methyl protons), 5.05 (1 H, quartet due to methine proton), 7.4–7.7 (multiplet due to phenyl protons), 8.0–8.3, and 9.17 ppm (due to substituted phenyl group protons).

Anal. Calcd for $C_{15}H_{12}SN_2O_5$: C, 54.21; H, 3.64; S, 9.65. Found: C, 54.15; H, 3.78; S, 9.73.

1-Phenyl-*cis*- and -*trans*-1-chloro-2-(2,4-dinitrophenylthio)propene (3 and 4). To 4.0 g (0.02 mol) of PCl_5 dissolved in 30 ml of CCl_4 by heating was added dropwise a solution of 3.0 g (0.0094 mol) of 2-(2,4-dinitrophenylthio)propiophenone dissolved in 20 ml of ethylene chloride. The solution was refluxed for 24 hr. After cooling to room temperature, the reaction mixture was washed with 50 ml of water and dried over anhydrous Na_2SO_4. The organic layer was filtered to remove unreacted sulfide. The product was irradiated to increase the amount of *cis* isomer. The isomers were separated on a 2% $AgNO_3$ alumina column by eluting with pentane followed by carbon tetrachloride, 50% carbon tetrachloride–benzene, and finally benzene. The *trans* isomer emerged when carbon tetrachloride was used as eluent, mp 160.5–161.5°; $\lambda_{max}^{95\%\ EtOH}$ 344 mμ (ε 9300); nmr 2.35 (3 H, singlet due to the methyl protons), 7.35 (5 H, due to the phenyl protons), and 7.5–9.6 ppm (3 H, due to the protons of the substituted phenyl ring).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 51.47; H, 3.43; Cl, 10.07.

The *cis* isomer emerged when benzene was used as eluent, mp 146.5–147.5°; $\lambda_{max}^{95\%\ EtOH}$ 340 mμ (ε 10,900); nmr 2.15 (3 H, singlet due to the methyl protons), 7.50 (5 H, due to the phenyl protons), and 7.2–9.2 (3 H, due to the protons of the substituted phenyl ring).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 51.51; H, 3.36; Cl, 10.19.

1-Phenyl-1-(2,4-dinitrophenylthio)propanone. To a solution of 5.0 g (0.02 mol) of 2,4-dinitrobenzenesulfenyl chloride in 50 ml of glacial acetic acid was added dropwise a solution of 6 ml (0.045 mol) of phenylacetone in 10 ml of acetic acid, with stirring. The solution was heated gently (40–50°) for 30 hr until a starch–iodide test was negative. The reaction mixture was cooled, and ice water (50 ml) was added to the solution, causing a brown oil to form. The solvent was removed on a rotary evaporator. The oily residue was dissolved in acetic acid, with the exception of a brown solid that was collected by suction, mp 270°. Its infrared spectrum showed this solid to be the disulfide.

The acetic acid was again removed under vacuum on a rotary evaporator, and the resulting oil was dissolved in methanol. The solution was concentrated, causing yellow crystals to form, mp 123–126°. The solid was recrystallized from methanol to give 2.0 g of product, mp 126.5–128°, yield 28%; $\gamma_{C=O}^{KBr}$ 1718 cm^{-1}; nmr 2.27 (3 H, singlet due to methyl protons), 5.45 (1 H, singlet due to

(20) C. D. Hurd and A. Tockman, *ibid.*, **23**, 1087 (1958).
(21) D. D. Lawson and N. Kharasch, *ibid.*, **24**, 858 (1959).

methine proton), and 7.3–9.5 ppm (peaks due to phenyl and substituted phenyl protons).

Anal. Calcd for $C_{15}H_{12}SN_2O_5$: C, 54.21; H, 3.64; S, 9.65. Found: C, 54.52; H, 3.99; S, 9.68.

1-Phenyl-*cis*- and -*trans*-2-chloro-1-(2,4-dinitrophenylthio)propene (5 and 6). To a solution of 1.0 g (0.005 mol) of PCl_5 dissolved in 20 ml of CCl_4 was added dropwise a solution of 0.05 g (0.0016 mol) of 1-phenyl-1-(2,4-dinitrophenylthio)propanone in 20 ml of ethylene chloride. The solution was refluxed for 48 hr, cooled, and then washed with 50 ml of water. The organic layer was dried over anhydrous $MgSO_4$, concentrated, and placed onto a 1% $AgNO_3$–alumina column which was eluted with CCl_4. Six fractions were collected, and the solvent was removed by evaporation in a stream of air. The first fraction which contained pure *trans* isomer was recrystallized from methanol, mp 116–117°; $\lambda_{max}^{95\%\ EtOH}$ 340 mμ (ε 14,900); nmr 2.67 (3 H, singlet due to methyl protons) and 7.5 ppm (multiplet due to protons of phenyl and substituted phenyl groups).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 51.00; H, 3.08; Cl, 10.27.

Repeated chromatography on a 1% $AgNO_3$–alumina column provided a sample of the pure *cis* isomer; $\lambda_{max}^{95\%\ EtOH}$ 341 mμ (ε 13,200); nmr 2.42 (singlet due to methyl protons) and 7.3–9.5 ppm (scattering of peaks, due to phenyl and substituted phenyl protons).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 50.98; H, 3.31; Cl, 9.99.

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride and 1-Phenylpropyne. To a solution of 0.63 g (0.0026 mol) of 2,4-dinitrobenzenesulfenyl chloride in 10 ml of chloroform was added dropwise 0.27 g (0.0024 mol) of 1-phenylpropyne. The reaction vessel was covered with tin foil and was placed in a constant temperature bath at 50.98°. When the starch test was negative, the reaction vessel was removed from the bath, and the solvent was removed on a rotary evaporator.

A sample of known weight of the reaction mixture was placed on an alumina column and was eluted with CCl_4. A single yellow band was collected. The sample was taken to dryness by evaporation in a stream of air. The solid was weighed and its nmr spectrum was then recorded.

Using mixtures of known composition, it was demonstrated that no significant product fractionation occurs during the isolation process.

No difference in product composition was observed when the reaction was carried out in the presence of added oxygen or in the presence or absence of light.

Product Stability. A 0.0958-g sample of known composition of **3**, **4**, **5**, and **6** (122:8:13:12, respectively) was placed in 10 ml of chloroform containing 0.010 g of 2,4-dinitrobenzenesulfenyl chloride. The solution was allowed to stand for 3 days at 50.98°. Upon removal of the solvent, the nmr spectrum was recorded and showed the original composition.

Kinetic Studies. Solutions of 2,4-dinitrobenzenesulfenyl chloride and 1-phenylpropyne in chloroform were prepared by weight. The reaction solutions were prepared by adding the sulfenyl chloride solutions to the acetylene solution, both being preequilibrated at the bath temperature (50.98 ± 0.02°). Aliquots (0.5 ml) were withdrawn at intervals and were stored at −25° until the reaction was complete. The nmr spectra of all the samples were recorded and integrated in the region 2–3 ppm. The data for one typical run are shown in Table III.

Table III. Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with 1-Phenylpropyne in Chloroform at 50.98 ± 0.02°

Time × 10^4, sec	Concn of acetylene[a] (a_T), mol/l.	$1/a_T$, l./mol	$(1/a_T) - (1/a_0)$, l./mol	$k \times 10^4$, l. mol^{-1} sec^{-1}
0	0.181	4.98	0	
0.36	0.179	5.59	0.61	(1.69)[b]
1.62	0.141	7.09	2.11	1.30
2.16	0.131	7.65	2.67	1.23
3.24	0.119	8.42	3.44	1.06
3.78	0.111	9.04	4.06	1.07
8.64	0.0683	14.62	9.64	1.11
9.90	0.0644	15.54	10.56	1.07
10.80	0.0603	16.58	11.60	1.07
17.28	0.0402	24.87	19.89	1.15
			Mean k	1.13

[a] Both reactants were at equal initial concentrations. [b] Values in parentheses were neglected in calculating the mean value of k.

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Kinetics of the Reaction of *p*-Benzoquinone with Sodium Thiosulfate

Yoshiro Ogata, Yasuhiko Sawaki, and Sumio Gotoh

Contribution No. 106 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.
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Abstract: The reaction of *p*-benzoquinone with sodium thiosulfate has been kinetically studied in aqueous and aquoethanolic solutions. The reaction at pH 1–5 gives a quantitative yield of hydroquinonethiosulfuric acid, while the reaction at pH above 5.6 accompanies hydroquinone and other products together with it. The reaction follows second-order kinetics in the range of pH 2–5, E_a and $\Delta S^{\mp}$ being 4.0 kcal/mol and −39 eu, respectively. The rate is affected by the acidity of the media, showing general acid catalysis. The rate is considerably accelerated by increasing the content of ethanol in the solvent. These results are discussed in terms of nucleophilic addition of thiosulfate ion.

The reactions of quinones with thiol compounds have been the subjects of many investigators who have shown the reaction products to be hydroquinones and/or their addition compounds with thiols.[1–6] However, the mechanism of the addition is still obscure, although

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