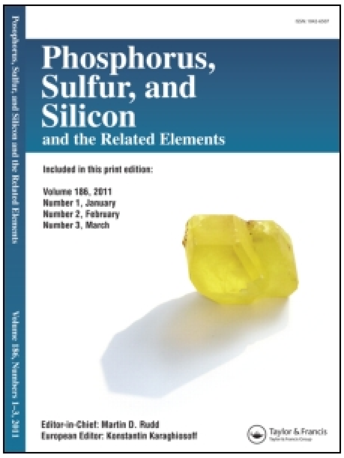

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POLAROGRAPHIC STUDY OF STRUCTURE-PROPERTIES RELATIONSHIP OF *p*-TOSYL SULFILIMINES

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POLAROGRAPHIC STUDY OF STRUCTURE-PROPERTIES RELATIONSHIP OF *p*-TOSYL SULFILIMINES

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A structure-reactivity relationship for a series of eight *N*-*p*-tosyl sulfilimines and five related sulfoxides is investigated by polarographic reduction of the S–N and S–O bonds respectively. Conjugation of the tricoordinated sulfur is the dominant factor that controls the rate of the S–N and S–O bond cleavage, which follows a trend opposite to that of the oxidation process. A significant correlation between the $E_{1/2}$ values and the ν_{S-N} IR frequencies is presented.

Key words: Dibenzothiophene *N*-*p*-toluenesulfonylsulfilimine; polarography; sulfoxides; sulfilimines, *N*-*p*-toluenesulfonyl; IR spectra; reduction potential.

INTRODUCTION

Oxidations of sulfur[1] in the reactions of the type (1) with rate constants k_1 are strongly susceptible to substituent effects.[2-13]

$$>S + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} >S - X \qquad (1)$$

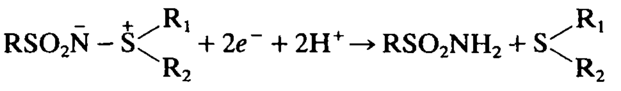
(where X = O, alkyl or *p*-tosylamido group).

Sulfur conjugation is considered to be the major factor controlling the reaction rates of oxidation to the respective sulfoxides. This effect is most marked when the sulfur atom participates in an aromatic π-electron system. In such cases the susceptibility of the rates to substituent effects reach extreme values reflecting the exceptionally low nucleophilicity of the sulfur atom. Thus, the difference in the oxidation rate between dibenzothiophene and diphenyl sulfide to the corresponding sulfoxides can reach up to two orders of magnitude depending on the conditions.[5,6] Changes in susceptibility resulting from substitution at the thiophenoid sulfur (as determined via X-ray crystallographic data in selected sulfoxides and S-methyl thiophenium tetrafluoroborate) were attributed[14] either to a substantial decrease or loss of aromaticity in the product or, eventually, to its antiaromatic destabilization.

For the reduction of the tricoordinated derivatives of sulfides with rate constant k_{-1} no systematic structure-reactivity relationship studies have been reported. It can be assumed that the reduction of thiophene derivatives (such as S-oxides, S-alkyl ions and *N*-*p*-tosylsulfilimines) will be facilitated by the aromatic character of the thiophene formed by applying the principle of microscopic reversibility.

To investigate the structure-reactivity relationship for a group of sulfilimines, polarographic half-wave potentials that involve the reductive cleavage of the S–N bond were chosen in this study. The selected sulfilimines represent compounds whose parent sulfide belongs to one of the following five categories: a) aromatic sulfur heterocycles (dibenzothiophene, **1**), b) non-aromatic sulfur heterocycles (phenoxathiine, **2** and thianthrene, **3**), c) diaryl sulfides (diphenyl, **5** and bis-*p*-methoxyphenyl sulfide, **6**), d) aryl alkyl sulfides (thioanisole, **4**), and e) dialkyl sulfides (dibenzyl, **7** and dimethyl sulfide, **8**). The compounds and their physical properties are listed in Table I.

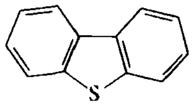
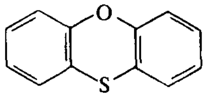
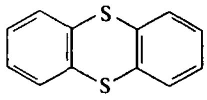
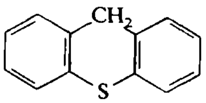
Sulfilimines were reported to be reduced at the dropping mercury electrode (DME) in aqueous[15] and aprotic[16] media in a single two-electron wave, which results in the S–N bond cleavage. The electrode process (2) is irreversible, diffusion controlled, and both products, the respective sulfide and *p*-toluenesulfonamide, have been isolated and identified.[15]



$$\mathrm{RSO_2\overset{-}{N}-\overset{+}{S}}\begin{smallmatrix}\mathrm{R_1}\\ \mathrm{R_2}\end{smallmatrix} + 2e^- + 2\mathrm{H^+} \rightarrow \mathrm{RSO_2NH_2} + \mathrm{S}\begin{smallmatrix}\mathrm{R_1}\\ \mathrm{R_2}\end{smallmatrix} \tag{2}$$

TABLE I

Physical constants of sulfilimines and sulfoxides

Compound	Parent Sulfide	Sulfilimine mp°C (lit)	Sulfoxide mp°C (lit)	ν_{S-N} (IR) (cm^{-1})
1		171 (171)	184 (190)	901
2		171 (168)	153 (153)	923
3		167 (169)	—	924
4	$CH_3SC_6H_5$	130 (132)	—	935
5	$C_6H_5SC_6H_5$	111 (113)	72 (72)	955
6	$(p\text{-}CH_3OC_6H_4)_2S$	134 (134)	—	960, 970
7	$(C_6H_5CH_2)_2S$	191 (191)	—	978
8	$(CH_3)_2S$	158 (159)	liquid	938
9		—	111 (111)	—

The half-wave potentials of aqueous solutions of sulfilimines were found to be pH dependent;[15] thus, it was necessary to follow the pH effect on individual waves in order to find pH values at which it is possible to compare the structural effects on $E_{1/2}$. The structure-activity correlation of *p*-tosylsulfilimines was further extended to five structurally related sulfoxides; this allows a comparison of these two series with respect to the structural effect on the cleavage of the respective S–X bond. Furthermore, an IR study of the S–N frequencies allowed the correlation of $E_{1/2}$ values with $\nu_{S\text{–}N}$ absorptions.

The majority of the sulfilimines were prepared by means of the chloramine-T method.[8,17] Dibenzothiophene has been reported as non-reactive towards chloramine-T,[18] even though no problems were reported in the synthesis of the sulfoxides and sulfonium ions from this thiophene-like molecule.[14] Recently the dibenzothiophene derivative was prepared in our laboratory by two different methods: via a modified chloramine-T method (described in this publication) and a copper-catalyzed tosyl azide method.[19] However neither method was applicable to benzo[b]thiophene which bears an even less nucleophilic sulfur.

EXPERIMENTAL

P-Tosylsulfilimines were generally prepared via the widely used chloramine-T method.[8,17] Melting points and IR data are listed in Table I.

p-Toluenesulfonylsulfilimine of dibenzothiophene (**1**). Dibenzothiophene (**1**, 1.8 g, 0.020 moles) was dissolved in dry methanol (30 mL) and the solution was stirred in ice. To this a methanol (25 mL) solution of chloramine-T hydrate (6.5 g, 0.028 moles) in acetic acid (1 mL) was added dropwise with constant stirring. The sulfilimine started precipitating after a few minutes. Stirring was continued for two hours at room temperature, after which the product was filtered and recrystallized from chloroform: cyclohexane (1 : 1), mp 171° (60%).

IR (KBr): 3050 (C—H aromatic), 2910 (C—H aliphatic), 1590, 1495 (C—C aromatic), 1445 (CH_3), 1295 (SO_2, unsym), 1140 (SO_2, sym), 901 (>S—N), 810 (*p*-subst.). PMR ($CDCl_3$): 7.9–7.3 ppm (m, 12H), 2.5 ppm (s, 3H). C^{13} NMR ($CDCl_3$): 142.03, 141.26, 137.13, 137.05, 132.96, 129.91, 129.26, 127.25, 126.51, 122.52, 21.40. MS *m/e* (rel. intensity): 353 (P^+, 5), 184 (100), 155, 139, 91.

In the preparation of sulfoxides, both dibenzothiophene (**1**) and phenoxathiine (**2**) were oxidized with hydrogen peroxide in acetic acid according to Gilman and Esmay,[20] but only two-thirds of the recommended quantity of hydrogen peroxide was used to minimize the amount of sulfone produced. Thioxanthene (**9**) was oxidized to its sulfoxide via *m*-chloroperbenzoic acid in methylene chloride,[21] while diphenyl sulfoxide (**5b**) was obtained from Aldrich Chemical Co. and dimethyl sulfoxide (**8b**) from Fisher.

All polarographic studies were done using an IBM 225[1A] Voltametric Analyzer with IBM 7424MT X–Y–Z Recorder and a three electrode system with a saturated calomel reference electrode. The dropping mercury electrode had natural drop-time $t_1 = 3.5$ s and was used with a controlled drop-time $t_1 = 0.4$ s. The rate of voltage scanning was 420 mV/min.

1–2 × 10^{-3} M stock solutions of compounds **1a–9a** and **1b**, **2b**, **5b**, **8b** and **9b** were prepared in 95% aqueous ethanol. Aliquots of those stock solutions were added to solutions of acids as buffers so that the final concentration was approximately 2×10^{-4} M. The following solutions were used: 0.1 M aqeous HCl (pH = 1.2), 0.02 M aqeous H_2SO_4 (pH = 2.7), acetate (pH = 4.0), phosphate (pH = 6.8), and borate (pH = 8.4) buffers, as well as 0.1 M aqeous NaOH (pH = 12.7). The ionic strength of buffers used was about 0.1. Polarographic curves were recorded after deaeration at 25 ± 3°C. Unlike other *p*-tosylsulfilimines examined, the dibenzothiophene derivative **1a** underwent rapid hydrolysis at pH = 12.7, as indicated by the relatively rapid decrease of its reduction wave with time. This decrease was accompanied by an increase in the reduction wave of dibenzothiophene sulfoxide. Occurrence of the hydrolysis was confirmed by thin layer chromatography. Infrared spectra were taken on a Perkin Elmer 225 using KBr pellets.

RESULTS AND DISCUSSION

The half-wave potentials of sulfilimines are shifted to more negative values with increasing pH (Figure 1). At pH between 6.5 and 8.4 the half-wave potentials became pH independent (Table II). This indicates that the electron transfer is preceded by an acid-base equilibrium (3) which is rapidly established at pH lower than about 6. In acidic media a protonated form of the sulfilimine is reduced (4). at pH > 8 where the half-wave potentials are pH independent, it is the conjugate base (which predominates in this pH range in the bulk of the solution) that undergoes reduction (5).

$$>\overset{+}{S}—\overset{-}{N}\text{-Tos} + H^+ \rightleftharpoons >\overset{+}{S}—NH\text{-Tos} \qquad (3)$$

$$>\overset{+}{S}—NH\text{-Tos} + 2e^- \underset{E_1}{\overset{H^+}{\rightleftharpoons}} >S + H_2N\text{-Tos} \qquad (4)$$

$$>\overset{+}{S}—\overset{-}{N}\text{-Tos} + 2e^- \underset{E_2}{\overset{2H^+}{\rightleftharpoons}} >S + H_2N\text{-Tos} \qquad (5)$$

Transfers of additional protons in reactions (4) and (5) occur consecutive to the potential determining step. System (3)–(5) corresponds to an $E_{1/2}$ – pH plot with two linear segments (Figure 1). The value of pH corresponding to the intersection of the two linear segments is denoted as pK′ and its value is in accordance with

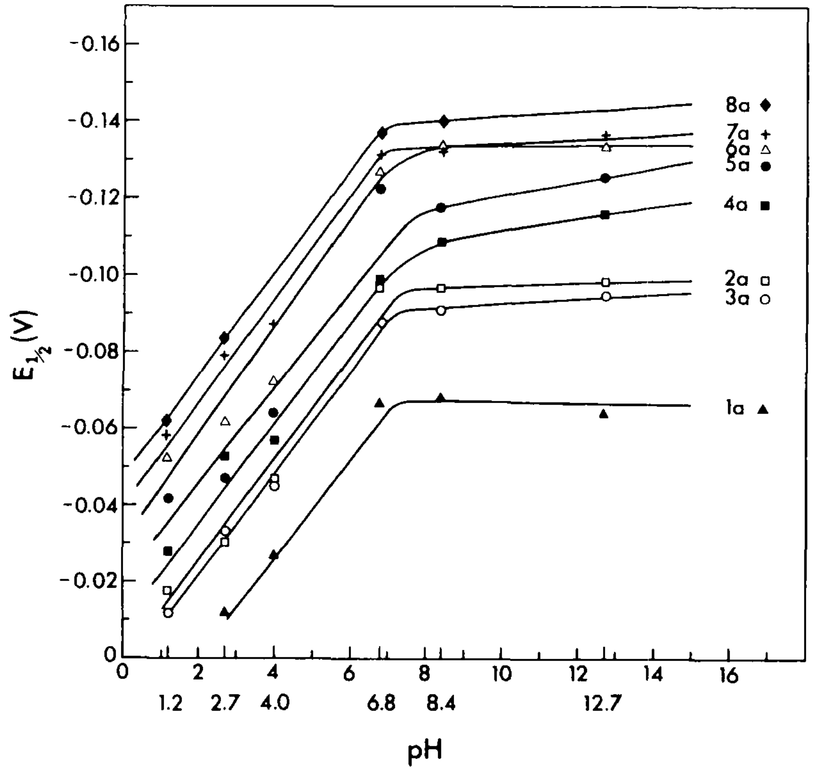


FIGURE 1 $E_{1/2}$ versus pH correlation of *p*-tosyl sulfilimines' polarographic reduction.

TABLE II

pH dependence of sulfilimines' reduction half-wave potentials (V vs. SCE)

Compound	pH						Corr. coeff.	
	1.2	2.7	4.0	6.8	8.4	12.7	a	b
1a	—	−0.123	−0.269	−0.670	−0.681	−0.639	0.997	0.944
2a	−0.176	−0.301	−0.473	−0.971	−0.968	−0.992	0.976	0.957
3a	−0.117	−0.324	−0.460	−0.881	−0.910	−0.952	0.996	0.973
4a	−0.280	−0.526	−0.563	−0.984	−1.085	−1.162	0.970	0.985
5a	−0.414	−0.468	−0.636	−1.228	−1.180	−1.250	0.932	0.922
6a	−0.526	−0.607	−0.712	−1.266	−1.339	−1.330	0.926	0.954
7a	−0.576	−0.794	−0.853	−1.309	−1.321	−1.362	0.975	0.959
8a	−0.614	−0.838	—	−1.367	−1.400	—	0.999	0.937

[a] pH range 1.2–6.8
[b] pH range 1.2–8.4

theory[22] considerably higher than the corresponding pK_a. For a change in mechanism at $pH > pK'$ the theory predicts the presence of two waves in the region of $pH = (pK' \pm 1)$. The separation of the two waves was nevertheless not observed, as evidently the potential E_1 in this pH range is too close to potential E_2.

The slope $d[E_{1/2}]/d[pH]$ at $pH < pK'$ varies between 130 and 142 mV/pH. The large value of this slope indicates that in addition to protonation occurring in a layer of the solution in the vicinity of the DME, the potential determining step is preceded by another protonation reaction occurring at the electrode surface.

Reduction scheme (3)–(5) postulates an ylide structure for the sulfilimines. This is in agreement with X-ray crystallographic data which indicate that even in the solid state the ylide, rather than the ylene form predominates.[3]

Absence of cross-over in the $E_{1/2} - pH$ plots for all investigated compounds (Figure 1) indicates that structural factors affect similarly potentials E_1 and E_2. Comparison of the half-wave potentials of the protonated form at $pH = 4.0$ and of the conjugate base at $pH = 8.4$ indicates that the values become more positive (and hence reduction enhanced) with increasing conjugation of the sulfur and reaches most positive value for the dibenzothiophene derivative.

It is impossible to treat the effect of groups attached to the sulfur in the studied reaction series of sulfilimines **1a**–**8a** by LFER. In such cases there are two alternative approaches: either to compare available data with these obtained by the same technique for a related reaction series or to compare the available data with data obtained for the same reaction series using another quantity characterizing reactivity changes with structure, involving the same reaction center.

Comparison of the first type is based on data observed for the reduction of sulfoxides derived from the same sulfides as for sulfilimines. In a way similar to sulfilimines, sulfoxides are reduced in one two-electron step at a pH lower than about 7 in the protonated form[22] and the $E_{1/2} - pH$ plots show two linear segments of different slopes (Figure 2). More negative values at $pH = 12.7$ indicate involvement of another acid-base equilibrium in alkaline solutions. For compounds derived from sulfides **1**, **2** and **5** an approximately linear relationship between the half-wave potentials of sulfilimines and sulfoxides (Figure 3) indicates a similar effect of conjugation on cleavage of the S—N and S—O bonds.

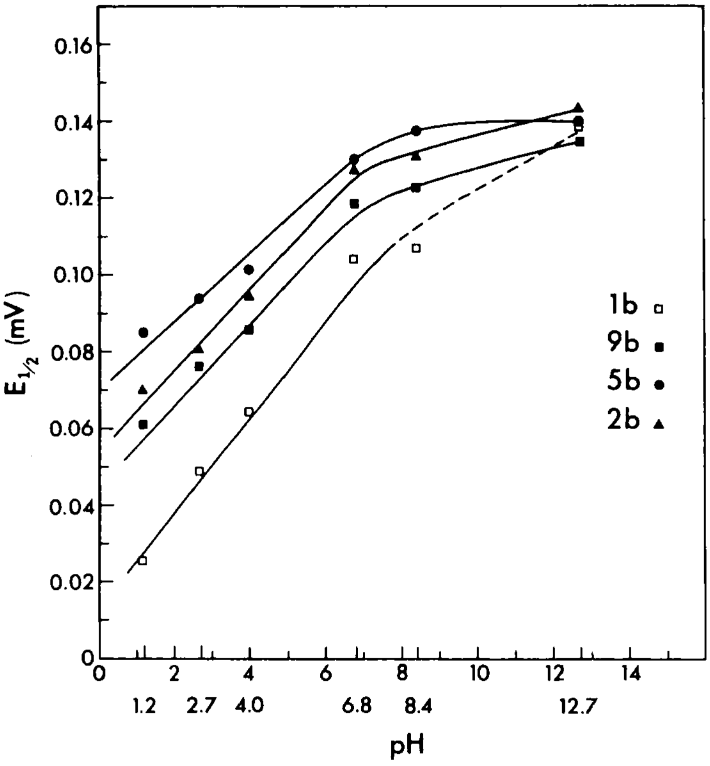


FIGURE 2 $E_{1/2}$ versus pH correlation of sulfoxides' polarographic reduction.

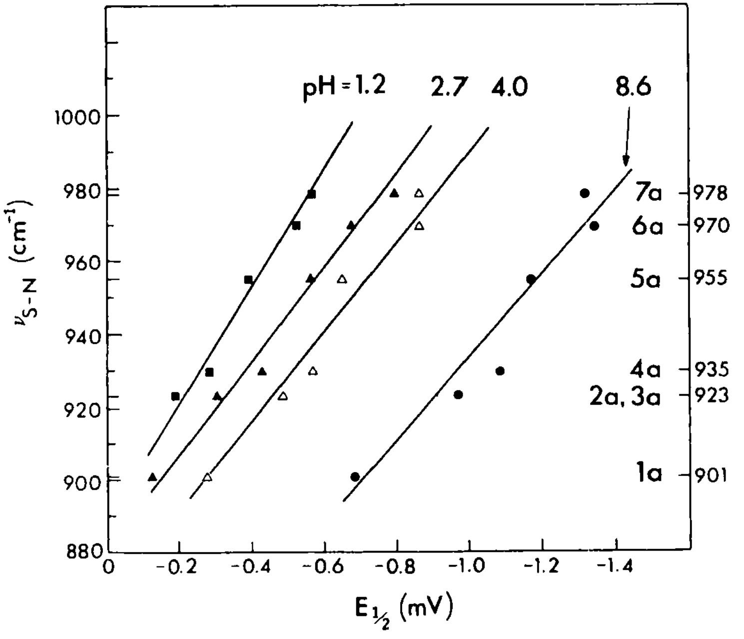


FIGURE 3 Polarographic $E_{1/2}$ versus IR ν_{S-N} for sulfilimines.

TABLE III

pH dependence of sulfoxides' reduction half-wave potentials (V vs. SCE)

	pH						Corr. coeff.	
Compound	1.2	2.7	4.0	6.8	8.4	12.7	a	b
1b	−0.254	−0.489	−0.635	−1.040	−1.071	−1.393	0.998	0.971
9b	−0.609	−0.766	−0.843	−1.191	−1.233	−1.345	0.987	0.977
2b	−0.702	−0.809	−0.944	−1.284	−1.309	−1.437	0.988	0.972
5b	−0.849	−0.941	−1.098	−1.291	−1.374	−1.391	0.987	0.987
8b	—	—	—	—	—	—	—	—

[a] pH range 1.2–6.8
[b] pH range 1.2–8.4

As expected, the presence of a methylene bridge in **9b** results in a structural effect similar to that of oxygen in **2b** (Table III).

Similarly the plots of half-wave potentials of sulfilimines at pH = 1.2 (corresponding to the reduction of the protonated form in (4)) and pH = 8.4 (reduction of the conjugate base in (5)) as a function of the frequency of the infrared absorption band of the S—N bond (Figure 3) show a linear correlation. This relationship indicates that a weaker S—N bond is reduced with lower activation energy in a trend similar to that found in the $E_{1/2}$ vs. $\nu_{C=O}$ relationship in a series of ketones and quinones.[23]

Finally it is possible to compare reduction (which involves a nucleophilic attack by an electron) to the rate of hydrolysis of the sulfilimine (a homogeneous nucleophilic process in which the hydroxide anion is the attacking agent). Dibenzothiophene sulfilimine (**1a**) has been shown to be the most reactive towards hydrolysis as it is towards the nucleophilic attack by electrons.

Based on the principle of microscopic reversibility, the oxidation of sulfides to sulfoxides should be affected by the structure of the sulfide in an opposite way when compared to the reduction of the S—X bonds. Attempts to correlate half-wave potentials of the S—N or S—O reduction with peak potentials for oxidation of sulfides to sulfoxides were complicated by the fact that the majority of the reported data was obtained in non-aqueous solvents,[24,25] where radical cations and dications rather than sulfoxides are formed. Available data for the oxidation of sulfides 1–8 were obtained, however in different solvents (80% acetic acid-water or methanol) and using different reference and supporting electrodes.[24,25] Thus, quantitative comparison of oxidation with reductions is not possible, but qualitatively it can be observed that dibenzothiophene **1** is least readily oxidized on a platinum anode[26] ($E_p = 1.44$ V versus SCE in 80% acetic acid, 0.18 M sulfuric acid) when compared to thianthrene[27] ($E_p = 1.10$ V versus Ag/AgCl in 80% acetic acid, 0.2 M $HClO_4$) and dialkyl and aryl alkyl sulfides[28] ($E_p = 0.84$ to 0.89 V versus SCE in methanol containing 0.1 M HCl). Thus, where oxidation is facilitated, reduction is made more difficult and vice versa.

Comparative studies of homogeneous oxidations using peroxidic reagents[4–7,10–13] did not include more than two of the sulfides **1–8** studied under the same conditions. Qualitatively, nevertheless, the oxidation kinetic data indicate a reverse trend to that of the electrochemical reduction values obtained (Table IV).

TABLE IV

Oxidation rate constants of sulfides to sulfoxides

	Parent sulfide				
Oxidation conditions	Benzothiophene	1	5	4	Ref.
$C_6H_5CO_3H/CH_2Cl_2/$ 20°C	—	0.057	10.70	—	5
$C_6H_5CO_3H$/dioxane: H_2O (1:1)/25°C	0.40	3.96	500	—	6
$H_2O_2/HClO_4$ (0.1 M)/ C_2H_5OH (25°C)	—	—	0.0095	0.0037	13

Thus, diphenyl sulfide (**5**) is oxidized more than a hundred times faster than dibenzothiophene by perbenzoic acid whether in dichloromethane[5] or dioxane/water (1:1).[6] Similarly, thioanisole (**4**) is oxidized three times as fast as diphenyl sulfide by acidified ($HClO_4$) hydrogen peroxide.[13] Interestingly enough the oxidation rate constant of benzo[b]thio-phene (**10**) is an order of magnitude smaller than that of dibenzothiophene, which is an indication of the poor nucleophilicity of the sulfur in the former species.

In conclusion this study on the polarographic reduction involving a series of sulfilimines and structurally related sulfoxides demonstrates the dominant role of conjugation on the reactivity at the tricoordinated sulfur atom. This also indicates that in the irreversible processes involved the transition state resembles the aromatic system. Unlike the sulfides and S-heterocycles in which rates of the reactions at the sulfur atom are decreased by conjugation of the S-atom the opposite effect, i.e. acceleration, is found for the structurally related S-derivatives in the reactions at the tricoordinated sulfur atom.

ACKNOWLEDGEMENTS

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