THE EFFECT OF SUBSTITUTION ON OXIDATION OF SULPHIDES

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Rates of oxidation of sulphur atom in diphenyl sulphide and dibenzothiophene derivatives by perbenzoic acid were determined. The effect of substitution was quantitatively interpreted by means of LFER relations, and from the dependences so obtained conclusions were drawn concerning electronic requirements of sulphur atom in transition state. The analysis of quantum chemical characteristics revealed that obtained data can be explained without assuming conjugation of sulphur $3d$ orbitals. The ϱ constants were quantitatively interpreted on the basis of perturbation theory of substituent effects.

Bonding characteristics of sulphur atom in various types of organic compounds are still the subject of experimental and theoretical studies, owing to possible participation of $3d$ or $4s$ orbitals[1-4] and that also in compounds of divalent sulphur. This possibility was first suggested by Pauling[3] in an attempt to explain observed dipole moment of thiophene, and since that time it has frequently been employed to account for differences in physical and chemical properties of sulphur compounds, compared to oxygen- or nitrogen-containing analogues. In previous works dealing with oxidation of sulphides[5-8] a striking fact was the decrease of oxidation rate by nearly two orders of magnitude when going from diphenylsulphide to dibenzothiophene. It seemed possible that the presence of the central thiophene ring changed qualitatively bonding characteristics of sulphur atoms. The experimental data so far reported were however incomplete and did not allow both series to be compared, not even qualitatively.

I   II

The aim of this work was to ascertain differences in bonding characteristics of sulphur atom by investigating substituent effects on the rate of oxidation of series of substituted diphenyl sulphides(I) and dibenzothiophenes(II) and to interpret these data in terms of MO theory.

EXPERIMENTAL

Compounds

Series of substituted diphenyl sulphides(I) and dibenzothiophenes(II), their preparation and physical properties are recorded in Table I. A more detailed description is given only when a new procedure or different method of isolation was employed. The purity of compounds was checked by thin layer chromatography (Silufol UV-254) or by gas chromatography (2% SE-30 silicone). Analytical samples were dried over P_2O_5 for 12 h, melting points were determined with a Boetius apparatus.

Diphenyl sulphide was prepared by reduction of diphenyl sulphoxide with zinc amalgam. The course of the reaction was followed chromatographically. After completion of the reaction the reaction mixture was diluted with water and diphenyl sulphide was taken into benzene. After drying the benzene was removed by distillation and diphenyl sulphide was distilled under reduced pressure. The product was obtained in 70% yield; m.p. 165°C/15 Torr, d_D^{20} 1·631) (ref.[9] b.p. 164°C/14 Torr).

Methyl diphenyl sulphide-3-carboxylate was obtained by esterification of the acid by diazomethane in ether. After solvent removal the ester was purified by distillation under reduced pressure. The pure product had b.p. 150—160°C/0·5 Torr. For $C_{14}H_{12}O_2S$ calculated: 68·85% C, 5·92% H, 13·11% S; found 68·90% C, 5·06% H, 12·88% S.

Perbenzoic acid was prepared from benzoyl peroxide and hydrogen peroxide[26]. After partial removal of the solvent chloroform, the solid peracid was precipitated by adding light petroleum. The acid was used as 10^{-4}M stock solution in dichloromethane; its content was determined by titration with thiosulphate.

Tetrabutylammonium perchlorate was obtained by precipitation of tetrabutylammonium bromide from its aqueous solution by perchloric acid. Traces of the bromide were removed by thorough washing with water. The perchlorate was dissolved in the necessary amount of isopropanol and reprecipitated by petrol. The pure perchlorate so obtained did not contain polarographically active admixtures.

Dichloromethane (Fluka) was used for kinetic measurements without further purification. It contained 0·03% water (by Fischer titration).

Measurements of Oxidation Rate

Rate of the oxidation of diphenyl sulphide and dibenzothiophene derivatives in dichloromethane at 20°C was measured polarographically, by following time dependence of the height of the wave corresponding to the peracid. Measurements were performe on a LP-55 polarograph equipped with an EZ-2 compensation recorder, using mercury droping electrode and reference 1M-calomel electrode. The capillary tube had time of drop 2·5 s at the mercury reservoir height 69 cm. The reaction was carried out directly in a temperature-controlled polarographic cell, which made it possible to record continuously the curves. Tetrabutylammonium perchlorate (0·05M) was used as an indifferent electrolyte. The temperature was kept with the accuracy of $\pm 0·1$°C. Under conditions of pseudomonomolecular reaction in an excess of sulphide, the rate constant of the oxidation to sulphoxide could be determined from the time dependence of the height of the wave of the peracid at limiting diffusion current potential ($-0·2$ V s.c.e.). Calculated rate constants are presented in Table I. Rates of oxidation of 4-nitro-4-acetamidodiphenyl sulphide and diphenyl sulphide-3-carboxylic acid could not be measured in this way, since the reduction wave of the sulphides occur in the region of limiting difussion current of the peracid.

RESULTS

Kinetic measurements. Results of kinetic measurements were interpreted by means of LFER relations. For series of diphenyl sulphides log k correlated with σ_m, σ_p, for dibenzothiophenes the rate data correlated with σ_p^+ substituent constants. Similar dependences on σ_p^+ were found for thianaphthenes by Kucharczyk[8]. Values of substituent constants were taken from ref.[27–30], with the exception of the σ_p and σ_m for COOH and COOCH$_3$ (ref.[23]), σ_p for C$_6$H$_5$CO (ref.[28]), σ_p^+ for C$_6$H$_5$CO which

TABLE I

Diphenyl Sulphides *I*, Dibenzothiophenes *II* and Rate Constants of Their Oxidation k_1 (in l mol^{-1} s^{-1}) by Perbenzoic Acid in Dichloromethane at 20°C

X	X′	M.p., °C	% S (calc./found)	Ref.	k_1
		Series *I*			
H	H	165/15^a	17·20/16·88	9	10·70
4-COCH$_3$	H	63—65	14·03/14·16	10	2·51
4-NO$_2$	H	54—55	13·85/13·88	11	0·99
3-COOCH$_3$	H	150—160/0·5^a	13·11/12·88	—	5·55
3-NHCOCH$_3$	H	83^b	13·17/12·49	12	7·76
4-NHCOCH$_3$	H	146	13·17/12·82	13	16·0
4-COC$_6$H$_5$	H	71	11·42/10·99	10	3·23
3-COOH	H	108—109	13·91/14·31	14	—
3-NO$_2$	H	40—41	13·85/14·11	14	1·20
4-Br	4-Br	115	9·30/ 9·81	15	3·16
4-NHCOCH$_3$	4-NHCOCH$_3$	214	10·66/10·87	16	25·8
4-COC$_6$H$_5$	4-C$_6$H$_5$CO	169	8·12/ 8·66	10	2·44
4-NO$_2$	4-NO$_2$	159—160	11·59/12·04	17	0·179
4-OCH$_3$	4-NO$_2$	69—70	12·26/12·83	18	5·40
4-NHCOCH$_3$	4-NO$_2$	193	11·11/11·34	19	—
4-N(CH$_3$)$_2$	4-NO$_2$	180^c	11·68/12·19	20	2·50
		Series *II*			
H		97—98	17·38/17·30	—	0·057
2-COC$_6$H$_5$	—	162—163	11·47/11·16	21	0·019
2-NHCOCH$_3$	—	177—178	13·27/13·10	22	0·132
2-Br	—	123—125	12·17/11·91	23	0·047
2-NO$_2$	—	186	13·97/13·89	23	0·014

^{a} B.p., °C/Torr; ^{b} *cf.* ref.[24]; ^{c} *cf.* ref.[25].
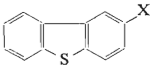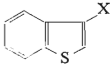
was read from the log k vs σ_p^+ dependence, and σ_p^+ for CH_3CO (ref.[8]). Reaction constants ϱ for corresponding reaction series are summarised in Table II.

Quantum chemical calculations. Calculations of series of substituted diphenyl sulphides and 2-substituted dibenzothiophenes were performed by HMO method with parameters for sulphur (p-model) $\alpha_s = \alpha - \beta$; $\beta_{cs} = -0.8\beta$. The value of the β_{cs} parameter -0.8 was used for comparison of obtained data with those reported by Kucharczyk, although Zahradník[31] considers as the best value -0.7. For further hetero atoms the parameters reported by Streitwieser[32] were adopted. The inductive model was used for methyl groups. Results of calculations are given in Table III. Substituent effect can be described by change of the α integral on the carbon bearing substituent. The effect of such a change on some quantum chemical quantities is demonstrated in Table IV.

DISCUSSION

Theoretical considerations. For purposes of comparison of quantum chemical data with the results of LFER correlation the perturbation theory was used to derive quantum chemical analogue of the Hammett equation. Similar equations were already reported.[33,34] Under verified assumption that log $k \sim \Delta E$ and $\Delta E = E_z - E_t$

TABLE II
ϱ Constants for Oxidation of Various Types of Sulphides to Sulphoxides

Substrate	Oxidizing agent/Solvent	ϱ
$4\text{-}X\text{—}C_6H_4SCH_3$	$HClO_4$/aq. C_2H_5OH (1 : 1)	-1.13^a
$4\text{-}X\text{—}C_6H_4SC_6H_5$	$HClO_4$/aq. C_2H_5OH (1 : 1)	-0.98^a
$4\text{-}X\text{—}C_6H_4SC_6H_5$	$HClO_4$/aq. C_2H_5OH (1 : 1)	-1.43
$4,4'\text{-}X\text{—}C_6H_4SC_6H_4\text{—}X$	$C_6H_5CO_3H$/CH_2Cl_2	-2.5
$4,4'\text{-}X\text{—}C_6H_4SC_6H_4\text{—}NO_2$	$C_6H_5CO_3H$/CH_2Cl_2	-0.94
	$C_6H_5CO_3H$/CH_2Cl_2	-0.77
	$C_6H_5CO_3H$/CH_2Cl_2	-2.65^b

^{a} Ref.[7]; ^{b} ref.[8].

(where E_z and E_t is the energy of the ground and of the transition state, respectively) and providing that $E_z = f(\alpha_i)$; $E_t = f(\alpha_i, \alpha_j)$, then in the second order approximation

$$\log k_i = -(q_j^0 \, \Delta\alpha_j + \tfrac{1}{2}\pi_{jj}^0 \, \Delta\alpha_j^2) + (\pi_{ij}^0 \, \Delta\alpha_j) \, \Delta\alpha_i , \qquad (1)$$

where q_j^0 is the electron density on the atom j in unsubstituted molecule and π_{ij}^0 is the atom-atom polarisability in unsubstituted molecule.

The energy of the initial state of a given molecule is changed only by substituent effect, while in the transition state the change is also due to the polarisation effect of approaching reagent.

Eq. (1) is formally identical with Eq. (2),

$$\log k_i = \log k_0 + \sigma_i \varrho \qquad (2)$$

when

$$\varrho \approx (\pi_{ij}^0 \, \Delta\alpha_j) ; \quad \log k_0 = -(q_j \, \Delta\alpha_j + \tfrac{1}{2}\pi_{jj}^0 \, \Delta\alpha_j^2) \qquad (3)$$
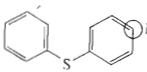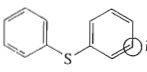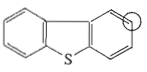
Table III

Quantum Chemical Data Calculated for Series I and II

$W\pi$ total electron energy (β), HOMO the energy of the highest occupied orbital (β), Q_s the electron density on sulphur, A_s the electrophilic localisation energy on sulphur (β), S_e/S electrophilic superdelocalisability on sulphur (β), π_{is} the c_i atom- S atom polarisability, i the position of carbon atom substituted with group X.

X	W_π	HOMO	Q_s	A_s	S_e/S	π_{is}
			Series I			
H	18·558	0·457	1·778	0·559	2·162	0·023[a]
4-NHCOCH$_3$	25·426	0·404	1·782	0·549	2·260	
4-COC$_6$H$_5$	30·721	0·489	1·742	0·594	2·003	
4-COCH$_3$	22·302	0·490	1·744	0·596	1·987	
4-NO$_2$	26·242	0·535	1·556	0·691	1·515	
			Series II			
H	19·055	0·571	1·728	0·672	1·740	0·0185[b]
2-NHCOCH$_3$	25·920	0·505	1·730	0·663	1·795	
2-COC$_6$H$_5$	31·208	0·596	1·708	0·698	1·661	
2-Br	22·086	0·561	1·729	0·670	1·750	
2-NO$_2$	26·680	0·615	1·625	0·745	1·448	

[a] $i = 4$; [b] $i = 2$.

TABLE IV

Dependence of Some Quantum Chemical Quantities on Changes of α_i

Compound	Quantity[a]	Donors $\leftarrow \Delta\alpha_i \rightarrow$ Acceptors				
		$+1$	$+0.5$	0	-0.5	-1
	W_π	17·713	18·087	18·558	19·131	19·796
	$HOMO$	0·337	0·399	0·456	0·502	0·535
	π_{is}	0·0128	0·0180	0·0232	0·0269	0·0281
	W	17·751	18·103	18·558	19·106	19·748
	$HOMO$	0·448	0·453	0·456	0·459	0·460
	π_{is}	0·00108	0·00078	0·00025	−0·00035	−0·00083
	W_π	18·212	18·586	19·055	19·624	20·285
	$HOMO$	0·436	0·509	0·571	0·612	0·634
	π_{is}	0·01139	0·01513	0·01858	0·0207	0·0209

[a] For meaning of symbols see Table III.

The effect of substituent is described only by change of α_i, which is equivalent to the requirement of proportionality of π-inductive and mesomeric effect and also to the requirement of proportionality of the effects of polarity and polarisability. In this approximation also substituent effect is additive.

The applicability of this approximation can be tested by the values of coefficient r, defined by Eq. (4), where ψ_i^L and ψ_i are HOMO's of the unsubstituted and substituted molecule, respectively and the summation over common atoms is denoted by asterisk. These coefficients are modified Polansky coefficients of similarity[35]

$$r = (\int \psi_i \psi_i^L \, d\tau)^2 = (\sum\nolimits^* c_{ij} c_{ij}^L)^2 \tag{4}$$

of course, only for similarity in frontier orbital. The importance of this orbital in the oxidation process under study will be demonstrated later. The values of r are for 4-substituted diphenyl sulphides:

X	H	NHCOCH$_3$	NO$_2$	COC$_6$H$_5$	COCH$_3$
r	1·000	0·928	0·637	0·930	0·926

and for 2-substituted dibenzothiophenes:

X	H	NHCOCH$_3$	NO$_2$	COC$_6$H$_5$	Br
r	1·000	0·870	0·776	0·933	0·985

Another test of applicability of this approximation will be described later in connection with the values of reaction constant ϱ and with the discussion of suitability of quantum chemical reactivity indices.

Mechanism of the oxidation. For quantitative examination of substituent effects the magnitude of ϱ constant provides most useful information which can be obtained from the Hammett equation. The negative value of ϱ obtained in this case confirms electrophilic character of the oxidizing agent, in agreement with the suggested mechanism[36−38]. The authors of the cited paper stress the importance of intramolecular hydrogen bridge of the peracid and report that on substitution of benzene for isopropanol as a solvent, $\Delta S^{\ddagger}$ of the oxidation of dibenzyl sulphide decreases by 8−12 e.u.
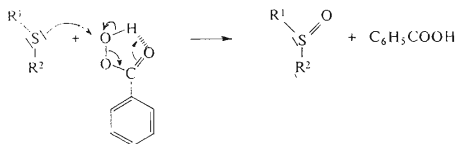

Table III presents the values of ϱ for oxidation of various types of organic sulphides. As follows from the data, ϱ is affected significantly not only by structural changes in substrate, but also by solvent. For that reason only values obtained under similar conditions can be discussed. As follows from Eq. (3)

$$\varrho_1/\varrho_2 = (\pi_{ij}\,\Delta\alpha_j)_1/(\pi_{ij}\,\Delta\alpha_j)_2 .$$

If $(\Delta\alpha_j)_2 = k(\Delta\alpha_j)_1$, then $(\Delta\alpha_s)_{DFS} = 1\cdot5(\Delta\alpha_s)_{DBT}$ and $(\Delta\alpha_s)_{DBT} \approx (\Delta\alpha_s)_{TN}$, where DFS, DBT, and TN denote successively diphenyl sulphide, dibenzothiophene, and thianaphthene.

The greater $\Delta\alpha_s$ for diphenyl sulphide corresponds to the greater disturbance of conjugation in the transition state of the oxidation of this substance relative to dibenzothiophene and thianaphthene. In the case of 4,4'-disubstituted diphenyl sulphides $\varrho_{4,4'} = 2\varrho_4$ (providing that substituent effects are additive). The value obtained $(-2\cdot5)$ is in fair agreement with the required value of $2\varrho_4$ $(-2\cdot86)$. This proves only

weak interaction of substituents through sulphur bridge and also justifies the description of substituent effect by change of α_i.

Correlation with quantum chemical data. The analysis of ϱ constants leads to conclusion that sulphur atom is less engaged in conjugation in transition state than it is in ground state, and that this effect is more pronounced for diphenyl sulphide than for dibenzothiophene. The measure of thechange of the extent of conjugation are the values of $\Delta\alpha_s$. Within the series, where constant $\Delta\alpha_j$ can be regarded as reasonable assumption (providing that approximation of substituent effect by change of $\Delta\alpha_i$ is correct), one can expect log k to correlate with the electron density on sulphur (q_s). Corresponding dependences for substituted diphenyl sulphides and dibenzothiophenes are graphically represented in Fig. 1. With substituted diphenyl sulphides, the linear correlation is well fulfilled, except the nitro derivative, whereas in the case of substituted dibenzothiophenes deviations from the linear dependence are observed with the nitro and acetamido derivatives. This can be understood on the basis of the coefficients of similarity which indicate the presence of electron-donor interaction in acetamido-benzothiophene. As to the nitro group, the description of its effect only by change of α_i is quite obviously little justified (compare the ratio of slopes of log k *vs* q_s plots for diphenyl sulphide and dibenzothiophene).

When comparing diphenyl sulphide and dibenzophenone derivatives, differences in mesomeric interaction of the reaction centre with substituent should be observed
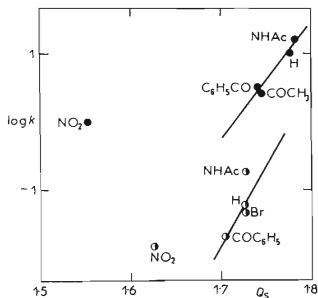

FIG. 1

Dependence of Oxidation Rate (log k) on Electron Density on Sulphur (Q_s) for 4-Substituted Diphenyl Sulphides (●) and 2-Substituted Dibenzothiophenes (◐)
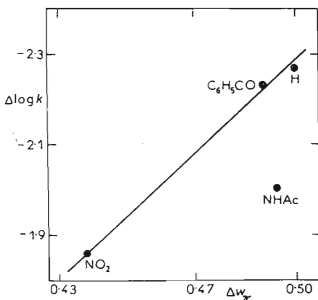
FIG. 2

The Δ log k *vs* ΔW_π Plot for Couples of Identically Substituted Dibenzothiophene and Diphenyl Sulphide Derivatives

for substituents with electron donor properties. The measure of such an interaction may be, for example, total π electron energy W_π. The inspection of the $\Delta \log$ . . k vs ΔW_π plots for dibenzothiophene and diphenyl sulphide derivatives reveals that it is the point for the acetamido derivative which does not lie on the regression line and also the direction of the deviation agrees with the above assumption (Fig. 2). This accounts also for different applicability of σ_p and σ_p^+ constants in Hammett correlations, since the difference between these constants is ascribed to such delocalisation effects[39]. As the calculations on substituted derivatives were performed with the use of the p-model for sulphur atom, it is further obvious that the observed facts can be explained without assuming the participation of sulphur d orbitals in conjugation. The perturbation theory also shows some limitations of the use of electron density (and, generally, all static indices) as the index of reactivity. In general, q_j can not be considered as reactivity index, since it has not the dimension of energy, and only the $q_j \Delta \alpha_j$ product can be taken as reactivity index, providing that first order perturbation theory is sufficient for describing the data. The q_j factor can be used as reactivity index only when $\Delta \alpha_j$ is constant. This might be the reason why reactivity data on aromatic hydrocarbons are grouped according to the position of substituents in their correlations with HMO data[37].

Log k's of series of diphenyl sulphide, dibenzothiophene, and thianaphthene derivatives correlate with energies of HOMO's (Fig. 3). Such correlations can be explained under the assumption that the reaction involves the excitation of ground state of the charge-transfer complex, the electron being transferred from the frontier orbital. From the grouping of data it is however evident that this electron transfer is not the
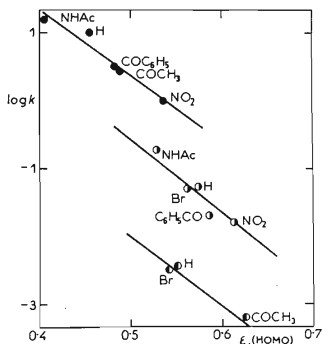

FIG. 3

Dependence of Oxidation Rate (log k) on Energy of the Highest Occupied Molecular Orbital (HOMO) for 4-Substituted Diphenyl Sulphides ($\bullet$), 2-Substituted Dibenzothiophenes ($\circlearrowright$), and 3-Substituted Thianaphthenes ($\circ$, see ref.[8])

only factor influencing the structure of transition state. The observed grouping of data can be removed by correlation equation of type (5) where $a = -4.58$, $b = -12.11$, and $c = 9.78$ (correlation coefficient 0.97). The form of Eq. (5)

$$\log k = a . \text{HOMO} + b . A_s + c \qquad (5)$$

allows to explain the grouping of reactivity data for aromatic hydrocarbons according to different positions by different values of $\Delta\alpha_j$. This grouping can be often avoided by the use of SCF reactivity indices. As already shown[39], the linear combination of HMO electrophilic localisation energy A_s with HOMO energy roughly equals the SCF localisation energy.

$$L^{\text{SCF}} = (a\ \text{HOMO} + b\ A_s) .$$

Hence, the observed dependence of oxidation rates (Eq. (5)) is equivalent to the equation

$$\log k = a'\ L^{\text{SCF}} + b' .$$

This result supports our suggestion that the grouping of reactivity data for aromatic hydrocarbons is due to different values of $\Delta\alpha_j$.

On the basis of these observations, the course of the oxidation under study can be depicted as follows:

$$\text{S} + \text{O}_x \;\rightleftharpoons\; (\text{S}...\text{OX}) \;\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\; (\text{S}^+...\text{O}_x^-) \;\overset{k_3}{\longrightarrow}\; \text{S} = \text{O} .$$

$$\text{CT complex} \qquad\qquad \text{excitation of CT complex}$$

The first step of the reaction can be regarded as the excitation of the ground state of CT complex, HOMO and A_s being related to k_1 and k_3 of the reaction scheme.

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