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OXIDATION OF ORGANIC SULPHIDES—XV[1]

STERIC EFFECTS ON THE ALKALINE OXIDATION OF SULPHOXIDES TO SULPHONES*

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Abstract—The oxidation of highly branched phenyl-alkyl and di-alkyl sulphoxides shows that in the alkaline oxidation steric hindrance has a more pronounced influence than in acidic oxidation, even if the steric effects are not very large. On the basis of these and previous results some suggestions on the geometry of the transition state of the alkaline oxidation are advanced.

It has been reported[2] that organic sulphoxides may be oxidized to sulphones by peroxyacids in alkaline media and that two different mechanisms—one electrophilic in character[3,4] and the other characterized by the nucleophilic attack of the peroxyacid anion on the SO group—are applicable.

In order to confirm the existence of the two reaction paths, a study of their steric requirements, which should be at least different in principle was undertaken.

In a preliminary study, the effect of *ortho* substituents on the oxidation of phenyl methyl sulphoxides with peroxybenzoic acid has been reported,[1] but the results do not characterize the two reaction paths on steric grounds on account of the small effects and the overlapping of polar factors. Consequently, more hindered systems such as phenyl-alkyl and dialkyl sulphoxides with highly branched alkyl chains have been prepared and their oxidation rates in alkaline and acidic media measured.

As the difference between the two reaction mechanisms was now quite definite, an hypothesis on the geometry of the transition states has been formulated.

RESULTS

The oxidation rates of phenyl-alkyl sulphoxides (I), and di-alkyl sulphoxides (II) in dioxan–water (40:60 and 50:50 in some cases) with peroxybenzoic acid in alkaline (apparent pH $\simeq$ 12) and acidic[5] media have been measured[2,3] (see also Experimental).

(I) Ph—SO—R R = Me, Et, n-Pr, n-Bu, i-Pr, t-Bu,
i-Bu and neo-Penthyl.

(II) R—SO—R′ R = R′ = Me, n-Bu, i-Pr, i-Bu, neo-Penthyl;
R = i-Bu and R′ = neo-Penthyl.

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* Work supported by National Research Council (C.N.R.).

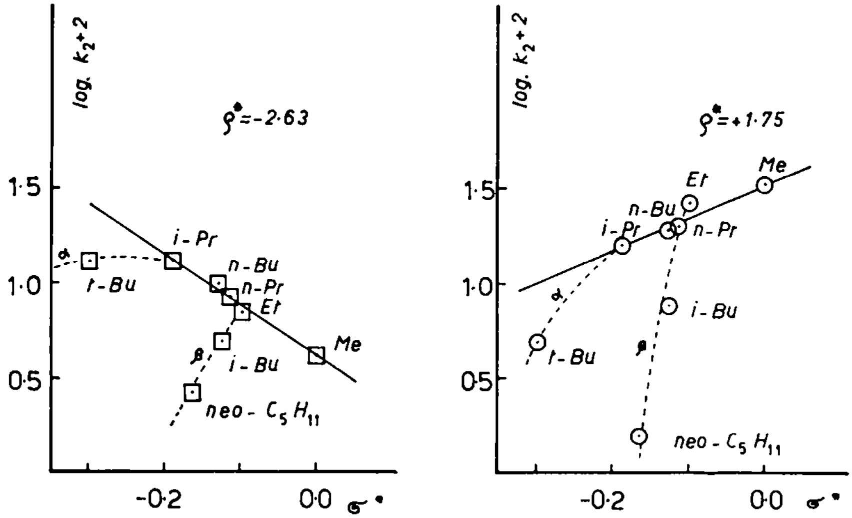
[1] Part XIV: D. Carnimeo and R. Curci, *Boll. Sci. Fac. Chim. ind. Bologna* in press.

[2] R. Curci and G. Modena, *Gazz. Chim. Ital.* **94**, 1257 (1964); *Tetrahedron Letters*, 1749 (1963); 863 (1965).

[3] G. Modena *et al.*, *Gazz. Chim. Ital.* **89**, 843 (1959); **90**, 3, 12 (1960); *Boll. Sci. Fac. Chim. ind. Bologna* **23**, 31 (1965); G. Kresze, W. Schramm and G. Cleve, *Chem. Ber.* **94**, 2060 (1961).

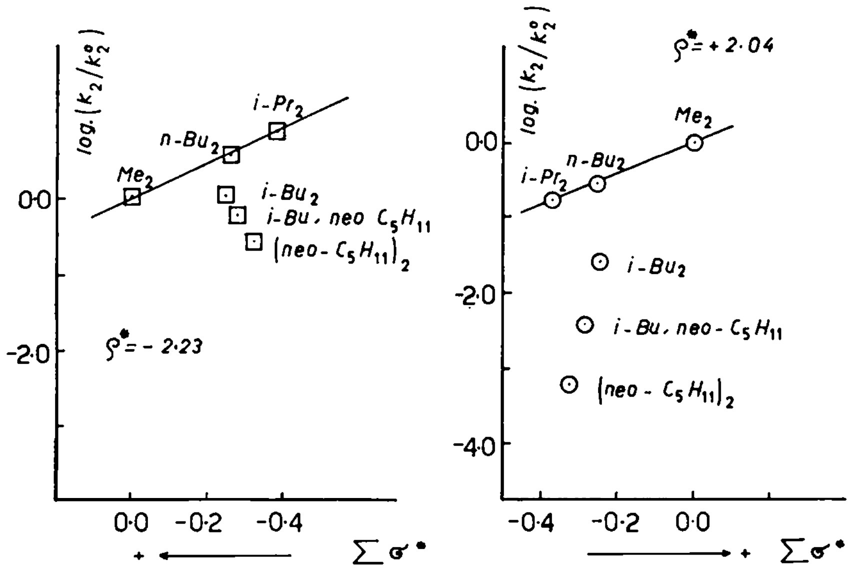
[4] D. Barnard, L. Bateman and J. I. Cunnen, *Organic Sulphur Compounds* (Edited by N. Kharasch) Vol. I, Chap. 21. Pergamon Press, London (1961); H. H. Szmant, *Ibid.* Chap. 16.

[5] The acidic medium in dioxan–water solution of the reagent (apparent pH 3·2–3·6). Our previous studies showed that in the pH ranges 4–6 and at pH higher than 11 there are not significant changes of the reaction rates with pH.



(a) (b)

Fig. 1. Oxidation rates of some phenyl alkyl sulphoxides at 25·0°: (a) acidic oxidation, in dioxan–water 50:50; (b) alkaline oxidation, in dioxan–water 40:60.



(a) (b)

Fig. 2. Rates of oxidation with PBA of some di-alkyl sulphoxides, in dioxan–water 40:60 at 25·0°: (a) acidic oxidation; (b) alkaline oxidation.

As shown by Robson *et al.*[6] and by Edwards *et al.*,[7] peroxybenzoic acid decomposes so slowly in alkaline solution, particularly at the high pH of our experiments, that this does not have a significant effect on many of the measurements. The oxidation rates of the more highly hindered compounds, however, are so slow that the autodecomposition of peroxybenzoic acid is no longer negligible and in these cases the reactions

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[6] J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.* **58**, 1846 (1962).

[7] E. Koubek, M. L. Haggett, C. J. Battaglia, Khairat M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *J. Amer. Chem. Soc.* **85**, 2263 (1963).

were performed in a large excess (20:1 or more) of the sulphoxide thus minimizing this side reaction. Although this technique appeared satisfactory for some intermediate cases, it was evident that in cases where the measured rates were very slow it was necessary to apply the following general kinetic law for the decomposition of peroxybenzoic acid:

$$(1) \qquad -\frac{d[RCO_3^-]}{dt} = k_1[SO][RCO_3^-] + k_2'[RCO_3H][RCO_3^-]$$

The accurate values of the rate coefficients were evaluated from (1) in its integrated form with the aid of an electronic computer (Experimental). The results are collected in Tables 1 and 2, and graphically in Figs 1 and 2.

TABLE 1. OXIDATION RATES OF SOME PHENYL ALKYL SULPHOXIDES WITH PBA, IN DIOXAN–WATER AT 25·0°

C_6H_5—SO—R		Dioxan–water 40:60		Dioxan–water 50:50	σ^{*e}
		alkaline react.[a]	acidic react.[b]	acidic react.[b]	
R = CH_3	10^2k	33·0	—	4·20[d]	0·000
C_2H_5	10^2k	27·0	—	7·00[d]	−0·100
C_3H_7(n)	10^2k	20·2	—	8·50[d]	−0·115
C_4H_9(n)	10^2k	18·8	—	9·70[d]	−0·130
C_3H_7(i)	10^2k	15·8	13·4	13·0[d]	−0·190
C_4H_9(t)	10^2k	4·84	13·5	13·0[d]	−0·300
C_4H_9(i)	10^2k	7·55	—	4·90[d]	−0·125
C_5H_{11}(neo)	10^2k	1·48[c]	2·40	2·70	−0·165
		$\rho^* = +1·75$ r = 0·94; s = 0·05		$\rho^* = -2·63$ r = 0·99; s = 0·03	

k in l mole^{-1} sec^{-1}.

[a] pH$_{app}$ = 12·00 ± 0·05 (Buffer: H_3BO_3/NaOH); EDTA added ca. 1–2 × 10^{-4} mole/l.

[b] pH$_{app}$ = 3·6–3·2

[c] evaluated for psuedo-first order runs as k/[SO], for [SO]/[PBA] > 20/1.

[d] data reported by A. Cerniani, G. Modena and P. E. Todesco, *Gazz. Chim. Ital.* **90**, 3 (1960).

[e] Taft's σ^* values.

TABLE 2. OXIDATION RATES OF SOME PHENYL ALKYL SULPHOXIDES WITH PBA, IN DIOXAN–WATER 40:60 at 25·0°

Compound		Acidic medium[a]	Alkaline medium[b]	$\Sigma\sigma^{*e}$
Me_2SO	10^2k	3·66	49·9	0·000
n-Bu_2SO	10^2k	13·0	13·8	−0·260
i-Pr_2SO	10^2k	26·3	8·55	−0·380
i-Bu_2SO	10^2k	3·69	1·16[c]	−0·250
i-Bu-SO-C_5H_{11}(neo)	10^2k	2·00	0·194[d]	−0·290
(neo-C_5H_{11})$_2$SO	10^2k	0·89	0·031[d]	−0·330
		$\rho^* = -2·23$ r = 0·99; s = 0·03	$\rho^* = +2·04$ r = 0·99; s = 0·03	

k in l mole^{-1} sec^{-1}.

[a,b,c] see Table 1.

[d] evaluated as reported in the Appendix.

[e] calculated from Taft's σ^* values.

DISCUSSION

The results indicate that even in very hindered systems the rate is not very depressed, since there is only a factor of 10^2–10^3 between the velocities of the fastest and the slowest compound. Further, it is evident that α-substitution is less effective than β-substitution and that isopropyl derivatives follow the Taft polar equation[8] well both in alkaline and acidic media. As the "rho" of the two reactions are opposite in sign,[2] i.e. the isopropyl derivative is faster in acidic but slower in alkaline oxidation than the corresponding methyl derivative, significant steric effect in the isopropyl derivatives must be excluded. On the other hand the t-butyl derivatives are only a little slower than required by the Taft polar relationship.

The comparison, particularly evident in the di-alkyl sulphoxides, between the steric effects in the acidic and alkaline oxidation shows that the latter is more affected by steric hindrance than the former. A more striking comparison is made in Table 3, where the relative rates of butyl- and neopenthyl derivatives are reported. In these compounds the polar effects are similar and the differences in the relative rates are almost completely due to steric effects. A more sophisticated comparison is based on the general Taft's equation: $\log (k/k_0) = \rho^*(\Sigma\sigma^*) + \delta E_s$, where δE_s is—in log units—the overall steric effect free from polar contributions (Table 4). The stronger steric effect observed in the alkaline oxidation is not large when compared with steric effects observed in other systems.[9–12]

Table 3. Relative rates of oxidation of some di-alkyl sulphoxides

Substituents	$(n\text{-Bu})_2$	$(i\text{-Bu})_2$	i-Bu, neo-C_5H_{11}	(neo-$C_5H_{11})_2$
Acidic oxidation	100	28·3	15·4	6·8
Alkaline oxidation	100	9·06	1·40	0·11

Table 4

R—SO—R′ R	 R′	Acidic oxidation $(\delta E_s)^a$	Alkaline oxidation (δE_s)
Me	Me	0·00	0·00
n-Bu	n-Bu	−0·03	−0·03
i-Pr	i-Pr	+0·01	+0·01
i-Bu	i-Bu	−0·55	−1·08
i-Bu	neo-C_5H_{11}	−0·88	−1·82
neo-C_5H_{11}	neo-C_5H_{11}	−1·34	−2·55

[a] δE_s values have been calculated from Taft's relationship:

$$\delta E_s = \log (k/k_0) - \rho^*\sigma^*$$

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[8] R. W. Taft, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman), Chap. 13, J. Wiley, New York (1956).

[9] A. Fava and A. Iliceto, *J. Amer. Chem. Soc.* **80**, 3478 (1958), and related papers; see also: W. A. Pryor, *Mechanisms of Sulfur Reactions* pp. 48–57, 63. McGraw-Hill, New York (1962).

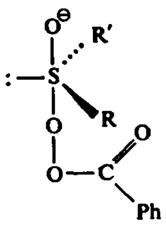
[10] W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.* **86**, 1150 (1964).

[11] K. Mislow, T. Simmons, J. T. Melillo and A. L. Ternay, *J. Amer. Chem. Soc.* **86**, 1452 (1964).

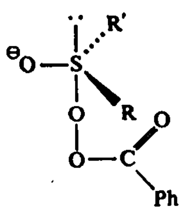
[12] D. Landini, F. Montanari, H. Hogeveen and G. Maccagnani, *Tetrahedron Letters* 2691 (1964).

The different steric requirements of the acidic and alkaline oxidations could be explained by different geometries of the transition states; although there is evidence that different degrees of bond forming might fit the experimental results equally well (see following paper).

The transition state of the acidic oxidation of sulphoxides with peroxyacids is usually described[3,4] as a more or less distorted tetrahedron where the oxidant attacks the lone pair on the sulphur atom. On the other hand in the alkaline oxidation, the definite nucleophilic character of the attack of the peroxyacid anion suggests that four groups and a lone pair of electrons must be arranged around the sulphur atom in the transition state. The most probable arrangement seems to be that of a more or less distorted trigonal bipyramid, as suggested by the known structure of SF_4[13] and similar derivatives of Se, P etc.[14,15] Accounting for the similar polar characteristics of the sulphoxidic oxygen, the lone pair, and the anionic oxygen, the following two structures may be considered:



III A



III B

A priori the two models do not seem very different in energy, but preliminary results,[16] as well as theoretical considerations make IIIA preferable to IIIB. On the other hand, based on the steric requirements of acidic and alkaline oxidations, the differences between IIIA and IIIB are not fundamental. Both formulations require that the attacking reagent makes a 90° angle with the R—S—R′ plane, while in the acidic oxidation, for which a "quasi" tetrahedral transition state is generally accepted,[3] the angle is about 109°. The difference in the angles bring about a difference in the distances between the organic residues (R) and the attacking reagent and consequently different steric effects. However, distortions of the bipyramid (see IIIA) structure tending to decrease the steric interactions are to be expected and the steric requirements of the two reactions may be smaller than the above limiting structures suggest.

Nevertheless the "alkaline" transition state should be more crowded than that of the acidic oxidation and therefore more sensitive to steric effects which is in agreement with the results now available.

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[13] W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.* **36**, 1119 (1962).

[14] J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.* **64**, 508 (1942).

[15] L. Horner and H. Winkler, *Tetrahedron Letters* 455, 3271, 3275 (1964); L. Horner and W. Hofer, *Ibid.* 3281, 4091 (1965).

[16] Preliminary experiments showed that the acidic and alkaline oxidations with PBA of an optically active sulphilimine ($R_1R_2S = NSO_2Ph$) yield the same optically active sulphoxyimine($R_1R_2S(O) = NSO_2Ph$) [see also G. Kresze and B. Wustrow, *Chem. Ber.* **95**, 2652 (1962)]. Model IIIB implies that the acidic and alkaline oxidations have opposite stereochemical courses, whereas model IIIA requires the same stereochemical course.

EXPERIMENTAL

Products

Sulphoxides. Most of the compounds, already described, were prepared and purified by standard methods and their physical constants agreed with reported values (Table 5). The unknown compounds were prepared as follows:

Table 5

Compound	M.p. °C	B.p. °C	Ref.
C_6H_5—SO—Me	30	144–145(15 mm)	*a*
C_6H_5—SO—Et	—	101–102(0·01 mm)	*b*
C_6H_5—SO—Pr(n)	—	102–103(0·005 mm)	*b*
C_6H_5—SO—Pr(i)	—	101–102(0·01 mm)	*b*
C_6H_5—SO—Bu(n)	—	114–115(0·01 mm)	*b*
C_6H_5—SO—Bu(i)	—	102–103(0·01 mm)	*b*
C_6H_5—SO—Bu(t)	57–58	—	*b*
C_6H_5—SO—C_5H_{11}(neo)	—	118–120(0·5 mm)	—
Me_2SO	—	87(18 mm)	*c*
n-Bu_2SO	31–32	140–142(20 mm)	*d, e*
i-Pr_2SO	—	96–97(15 mm)	*f*
i-Bu_2SO	67–68	—	*e*
i-Bu—SO—C_5H_{11}(neo)	66–67	—	—
(neo-C_5H_{11})$_2$SO	83–84	—	—

[a] G. Leandri, G. Mangini and R. Passerini, *J. Chem. Soc.* 1386 (1957).

[b] A. Cerniani, G. Modena and P. E. Todesco, *Gazz. Chim. Ital.* **90**, 3 (1960).

[c] Commercial product (Fluka), purified by several distillations under red. press.

[d] D. Edwards and J. B. Stenlake, *J. Chem. Soc.* 3272 (1954).

[e] D. L. Hammick and R. B. Williams, *J. Chem. Soc.* 211 (1938).

[f] P. Biscarini, G. Galloni and S. Ghersetti, *Boll. Sci. Fac. Chim. ind. Bologna* **21**, 154 (1963).

Phenyl neo-penthyl sulphoxide. Ethyl phenyl sulphinate (0·1 mole) in dry ether was reacted with neopenthyl magnesium bromide (0·11 mole) by heating under reflux.[17] The reaction mixture yielded 15·9 g (80%) crude phenyl neopenthyl sulphoxide and was purified by chromatography on alumina, b.p. 118–120°/0·5 mm Hg. (Found: C, 67·9; H, 8·20; S, 16·2. $C_{11}H_{16}OS$ requires: C, 67·3; H, 8·21; S, 16·3%.) The sulphoxide yielded on oxidation with peroxybenzoic acid *phenyl neopenthyl sulphone*, b.p. 99–101°/0·5 μ Hg. (Found: C, 61·7; H, 7·61; S, 14·9. $C_{11}H_{16}O_2S$ requires: C, 62·2; H, 7·60; S, 15·1%.)

Isobutyl neopenthyl sulphoxide. Was prepared by the reaction of *methyl isobutyl sulphinate* (b.p. 72°/15 mm Hg; Found: C, 44·8; H, 9·01; S. 23·1. $C_5H_{12}O_2S$ requires: C, 44·1; H, 8·88; S, 23·5%) with neopenthyl magnesium bromide as described, m.p. 66–67° from pet. ether. (Found: C, 61·9; H, 11·5; S, 18·0. $C_9H_{20}OS$ requires: C, 61·3; H, 11·4; S, 18·2%.) On oxidation it yielded *isobutyl neophenyl sulphone*, b.p. 97–98°/2 mm Hg. (Found: C, 56·7; H, 10·7; S, 16·6. $C_9H_{20}O_2S$ requires: C, 56·2; H, 10·5; S, 16·7%.)

Dineopenthyl sulphoxide was prepared by reaction of *methyl neopenthyl sulphinate* (b.p. 80°/12 mm Hg. Found: C, 47·2; H, 9·56; S, 20·7. $C_{16}H_{14}O_2S$ requires: C, 48·0; H, 9·39; S, 21·3%) with neopenthyl magnesium bromide; m.p. 82–83° from pet. ether. (Found: C, 63·2; H, 11·8; S, 16·8. $C_{10}H_{22}OS$ requires: C, 63·1; H, 11·6; S, 16·8%.) On oxidation it yielded *dineopenthyl sulphone*, m.p. 88–89° from pet. ether. (Found: C, 57·9; H, 10·7; S, 15·4. $C_{10}H_{22}O_2S$ requires: C, 58·2; H, 10·7; S, 15·5%.)

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[17] K. K. Andersen, *Tetrahedron Letters* 93 (1962); *J. Org. Chem.* **29**, 1953 (1964); K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley and R. I. Perkins, *J. Amer. Chem. Soc.* **86**, 5637 (1964).

Reagents and solvents. Peroxybenzoic acid[18] was prepared and purified and dioxan[19] purified by standard methods. A mixture of boric acid and NaOH (AnalaR products) was used throughout as buffer and the pH of the solution tested by a WTW pH-meter with glass electrode.

Kinetic method. The reactions solution were prepared as described[3] and the kinetic measurements based on iodometric titration of the peroxyacid. Concentrations of sulphoxide and peroxybenzoic acid were in the range 4–8 × 10^{-3} M, except when otherwise stated (see Tables). Buffer at 0·1 M concentration was used throughout and 1–2 × 10^{-4} M EDTA added for sequestering any heavy cations present.[6] The data reported in the Tables are average of at least two independent runs at different initial concentrations of the reagents; the rate coefficients were evaluated graphically by usual methods except for the very slow reactions (see Tables) when a more elaborated method was necessary (see Appendix).

Appendix. The general equation taking into account the two competitive reactions is:

$$(1) \qquad -\frac{d[RCO_3^-]}{dt} = k_1[RCO_3^-][R_2SO] + k_2'[RCO_3H][RCO_3^-]$$

At high and constant pH ($\simeq$12), $[RCO_3^-]$ is practically equal to the stoichiometric concentration. The second term of the Eq. 1, (k_2' $[RCO_3H][RCO_3^-]$), taking into account that the dissociated and undissociated peracid concentrations correlated by the K_a, become $k_2[RCO_3^-]^2$, where $k_2 = k_2'Y$ (and $Y = a_{H_3O^+}/K_a$). Consequently, (1) may be rewritten as:

$$(2) \qquad -\frac{d[RCO_3^-]}{dt} = k_1[RCO_3^-][R_2SO] + k_2[RCO_3^-]^2$$

To simplify the integration, the initial concentration of R_2SO may be taken as much larger than $[RCO_3^-]_0$ and therefore considered as constant. It follows that by substituting $[R_2SO]_0$ with "a", and $[RCO_3^-]$ with $(b - x)$, the Equation (2) gives after integration:

$$(3) \qquad \frac{b}{(b-x)} = e^{ak_1t} + \frac{bk_2}{ak_1}(e^{ak_1t} - 1)$$

The values of k_2 may be evaluated with good precision by independent measurements of the decomposition rate of peroxybenzoic acid at the given pH and the values of k_1 may be roughly estimated by the first 10–20% of reaction (in pseudo-first order conditions). The values of $b/(b - x)$ at various times are the experimental quantities against which the correct values of k_1 and k_2 which satisfy the equation are to be found: they are evaluated by successive approximation with the aid of an electronic computer (IBM 1620).[20]

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[18] A. Kerkomard and J. Bigou, *Bull. Soc. Chim. Fr.* 486 (1956).

[19] A. I. Vogel, *Practical Organic Chemistry* p. 177. Longmans Green, London (1956).

[20] Further details as well as the computer programme will be given on request.