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**Estimation of the rate constants for the reaction
of α - and β -endosulfan with OH radicals
by the incremental procedure of Atkinson**

by

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1 Introduction

The rate at which the OH radical reacts with organic compounds can be calculated by a system of increments, as shown by von Heicklen [1] via correlations with C-H bond dissociation enthalpies. These "structure activity relationships" (SAR) [2] are in the tradition of linear relationships of free energy (LFE) and were introduced by Atkinson for reactions with OH radicals [3].

If the OH rate constant is known, the formula:

$$-\frac{d[A]}{dt} = k_{rate} [OH] [A]$$

can be used to calculate the lifetime τ_A (or the half-life $t_{1/2} = \ln 2 \cdot \tau_A$) of substance A in the troposphere:

$$A = A_0 \cdot \exp(-t/\tau_A)$$

$$\tau_A = \frac{1}{k_{rate} \cdot [OH]}$$

The lifetime will be calculated here on the basis of a global OH concentration of $[OH] = 5 \cdot 10^5 \text{ cm}^{-3}$ [4, 5].

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The database available at present for reactions of OH radicals consists of over 500 measured rate constants [6], of which, according to the most recent publications, about 300 have been used for for parametrisation [7]. The calculated and measured rate constants agree in most cases within a factor of 2. Endosulfan has no aromatic properties; the rate constants of the reaction as a whole (k_{rate}) are calculated simply by addition (k_{add}) to double bonds and abstraction (k_{abs}) of hydrogen atoms:

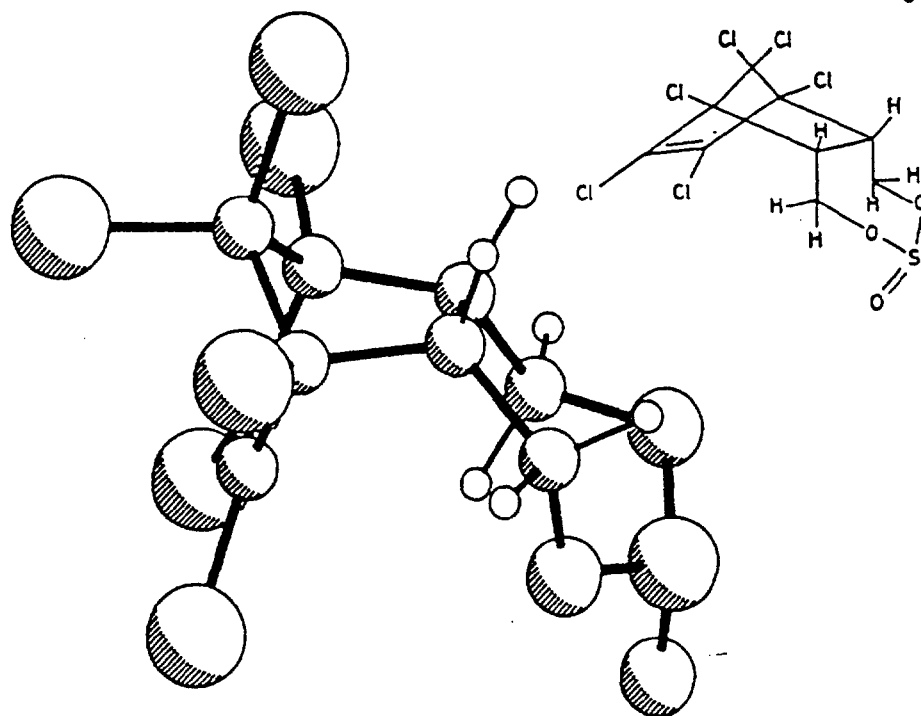
$$k_{rate} = k_{add} + k_{abs}$$

The various substituents at the reactive centres are allowed for by a multiplicative increment system concerned only with electronic, but not steric, effects. The following calculations relate to the data published by Atkinson in 1988 [7].

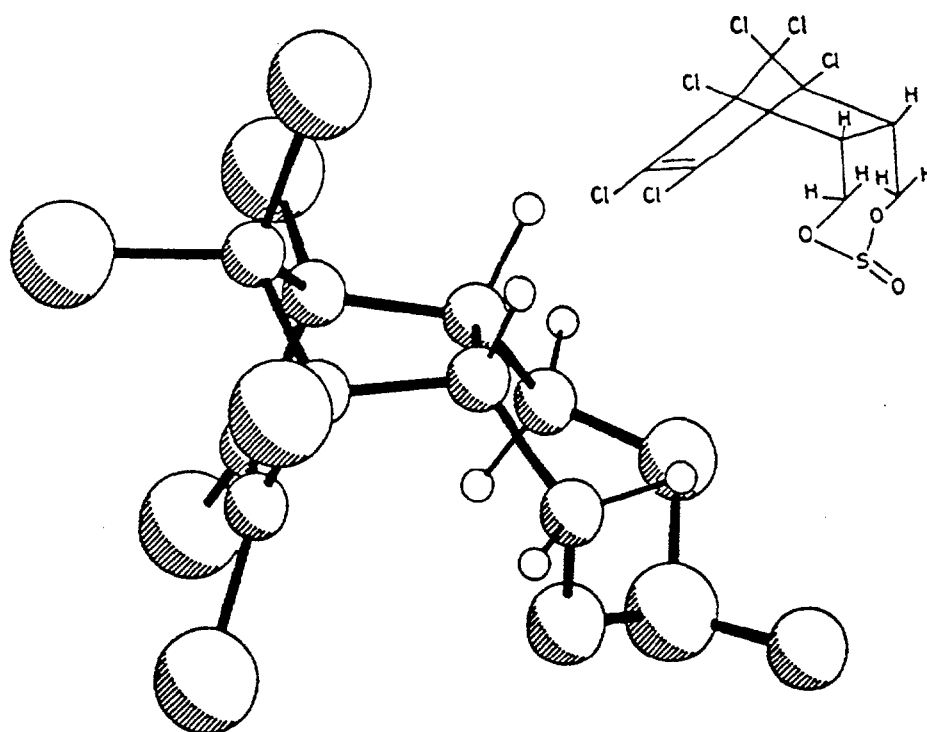
2 Calculation of rate constants k_{rate}

2.1 *The structure of α - and β -endosulfan*

To highlight any detectable steric effects, the structures of α - and β -endosulfan were optimised with the aid of an MM2 force field program as described by Allinger [8]. The structures thus obtained are shown in Fig. 1. The isomerism of α - and β -endosulfan results from the possible difference in position of the free electron pair on the sulphur atom and the consequent difference in the tetrahedral arrangement of the sulphite group.



α -ENDOSULFAN



β -ENDOSULFAN

Fig. 1:

Structures of α - and β -endosulfan calculated by force field program. For corresponding X-ray method, see [9].

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2.2 Calculation by the incremental system of Atkinson

2.2.1 Addition to the double bond

$$k_{\text{add}} = k_{\text{group}} \cdot F^2(x) \cdot F^2(y)$$

$$k_{\text{group}} = 11 \cdot 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

$$F(x) = F(\text{Cl}) = 0.2$$

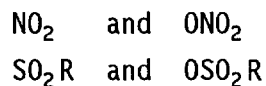
No parameters have been provided by Atkinson for $F(y)$. Instead, we suggest using a $-\text{CH}_2\text{Cl}$ group as increment and reducing $F(y)$ by an estimated factor of $2/3$ to allow for the influence of the chlorine substituents in the remaining part of the molecular structure:

$$F(y) = \frac{2}{3} \cdot F(\text{CH}_2\text{Cl}) = 0.76 \cdot \frac{2}{3} = 0.5$$

$$k_{\text{add}} = 11 \cdot 10^{-11} \cdot 0.2^2 \cdot 0.5^2 = 1.1 \cdot 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

2.2.2 Abstraction of hydrogen atoms

The available increments are also unsuitable for calculating abstraction, since the O-S(O)-O group is not parametrised. We therefore propose a comparison of the substituent pairs:



as the basis for a provisional estimation of the O-S(O)-O group.

If the parametrisation is a direct consequence of electronic effects, a correlation may be assumed to exist between the Atkinson increments and the inductive Hammett constants (σ_1). Fig. 2 (next page) shows this correlation for a number of substituents.

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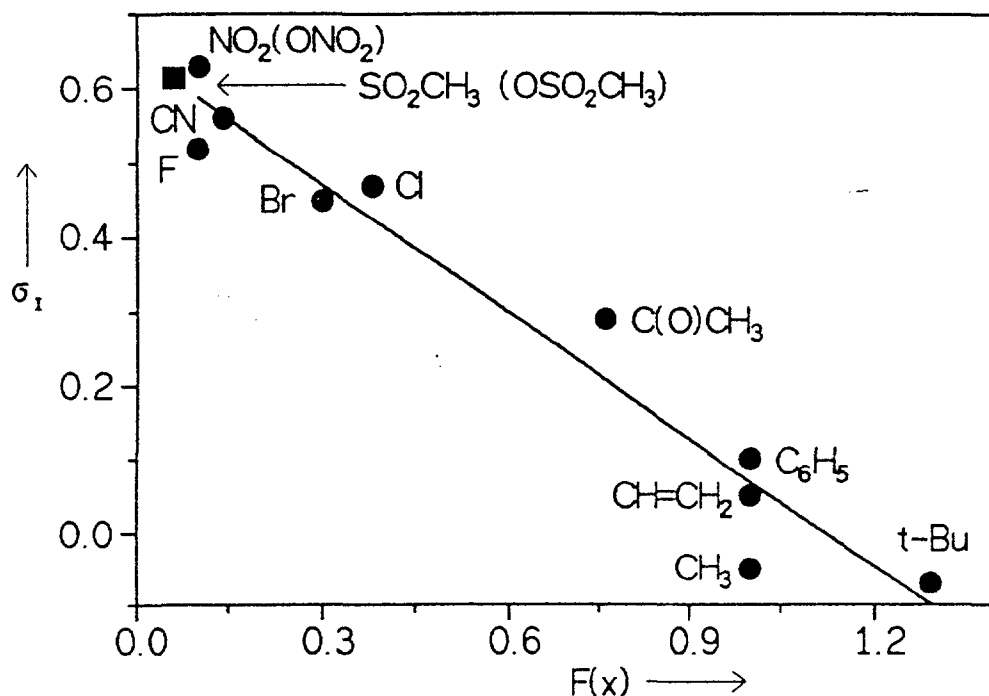
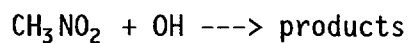


Fig. 2:

Correlation of the Atkinson increments [7] and the corresponding inductive Hammett constants [10].

The increment for the substituent ONO_2 is known to be $F(\text{ONO}_2) = 0.1$, and thus it is possible to calculate the (unknown) increment $F(\text{NO}_2)$, since, for example, the rate constant for the reaction



has been measured.

According to Atkinson, the increment $F(\text{ONO}_2)$ yields the rate constant:

$$k_{\text{abs}}(\text{CH}_3\text{ONO}_2) = k_0^{\text{p}} \cdot F(\text{ONO}_2)$$

$$k_{\text{abs}}(\text{CH}_3\text{ONO}_2) = 0.144 \cdot 10^{-12} \cdot 0.1 = 1.44 \cdot 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

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The rate constant $k_{\text{abs}}(\text{CH}_3\text{NO}_2)$ [6], in turn, yields

$$k_{\text{abs}}(\text{CH}_3\text{NO}_2) = 5.6 \cdot 10^{-19} \cdot T^2 \cdot \exp(-360/T) \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$$

resulting for $T = 298 \text{ K}$ in

$$k_{\text{abs}}(\text{CH}_3\text{NO}_2) = 1.48 \cdot 10^{-14} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$$

i.e. $F(\text{ONO}_2) \approx F(\text{NO}_2) = 0.1$.

By analogy, it may be assumed that

$$F(\text{SO}_2\text{R}) = F(\text{OSO}_2\text{R}).$$

Given the correlation between σ_1 and $F(x)$ shown in Fig. 2, the substituent SO_2R or OSO_2R (as model for the substituent $-\text{OS}(\text{O})\text{O}-$), with a value of $\sigma_1(\text{SO}_2\text{R}) = 0.62$, must be considered as a similarly strong electron attractant as the NO_2 group ($\sigma_1(\text{NO}_2) = 0.63$). This results in:

$$F(-\text{OS}(\text{O})\text{O}-) \approx 0.1$$

and for further calculation:

$$F(\text{CH}_2\text{ONO}_2) = 0.21 \approx F(\text{CH}_2\text{OS}(\text{O})\text{O}).$$

Abstraction of the "tertiary" hydrogen atoms:

$$\begin{aligned} k_{\text{abs}}^{\text{T}} &= K_{\text{O}}^{\text{T}} \cdot 2 \cdot F(x) \cdot F(y) \cdot F(z) \cdot F_{\text{ring}} \\ &= K_{\text{O}}^{\text{T}} \cdot 2 \cdot F(\text{CR}_2\text{H}) \cdot F(\text{CH}_2\text{Cl}) \cdot F(\text{CH}_2\text{OS}(\text{O})\text{O}) \cdot F(\text{pentacycle}) \\ &= 1.83 \cdot 10^{-12} \cdot 2 \cdot 1.29 \cdot 0.57 \cdot 0.21 \cdot 0.8 = 4.5 \cdot 10^{-13} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1} \end{aligned}$$

Abstraction of the "secondary" hydrogen atoms:

$$\begin{aligned} k_{\text{abs}}^{\text{S}} &= K_{\text{O}}^{\text{S}} \cdot 2 \cdot F(x) \cdot F(y) \cdot F_{\text{ring}} \\ &= K_{\text{O}}^{\text{S}} \cdot 2 \cdot F(\text{CR}_2\text{H}) \cdot F(\text{CH}_2\text{OS}(\text{O})\text{O}) \cdot F(\text{heptacycle}) \\ &= 0.838 \cdot 10^{-12} \cdot 2 \cdot 1.29 \cdot 0.1 \cdot 1 = 2.2 \cdot 10^{-13} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1} \end{aligned}$$

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2.3 Results

The total rate of OH reaction with endosulfan can be expressed as:

$$\begin{aligned} k_{\text{rate}} &= k_{\text{add}} + k_{\text{abs}}^{\text{T}} + k_{\text{abs}}^{\text{S}} \\ &= 1.1 \cdot 10^{-12} + 4.5 \cdot 10^{-13} + 2.2 \cdot 10^{-13} \\ &= 1.8 \cdot 10^{-12} \text{cm}^3 \text{ molecules}^{-1} \text{s}^{-1} \end{aligned}$$

Assuming the mean tropospheric concentration of OH radicals to be $[\text{OH}] = 5 \cdot 10^5 \text{ cm}^{-3}$, the half-life will be:

$$\begin{aligned} t_{1/2} &= \frac{\ln 2}{1.8 \cdot 10^{-12} \cdot 5 \cdot 10^5} = 7.3 \cdot 10^5 \text{ s} \\ &= 8.5 \text{ days} \end{aligned}$$

This result is subject to error by an estimated factor of approximately ± 10 , as will become evident from the discussion below.

2.4 Discussion

It must be assumed that the total rate k_{rate} is subject to error by a dimension upwards or downwards.

* In the case of k_{add} , this is due to insufficient information on the increments of the groups in the vicinity of the double bond and to the lack of information on the screening effects of the chlorine atoms in the bridge of endosulfan, which probably reduce the rate of addition.

* In the case of k_{abs} , it is due, as described above, to the approximative and provisional estimation of the increments

for abstraction of the hydrogen atoms on the corresponding tertiary or secondary carbon atoms. There is also the possibility that the hydrogen atoms should not be subdivided, as in the present calculation, into two equivalent groups, but rather into four differing groups, since the conformation of the heptacycle may be such as to exert an as yet unknown steric influence.

Atkinson's method of calculation yields the same rate for both isomers. There are, however, differences between α - and β -endosulfan, e.g. in melting point and vapour pressure:

	α -endosulfan	β -endosulfan	Lit.
Melting point ($^{\circ}\text{C}$)	106.5-109	210-211.5	[11]
Vap.pressure (25 $^{\circ}\text{C}$ /mbar)	$1.9 \cdot 10^{-5}$	$9.2 \cdot 10^{-7}$	[12]

These differences in the properties of the isomers are evidence of differences in the intermolecular Van der Waals interactions and hence of steric effects which may influence the reactivity of the hydrogen atoms, as has also been demonstrated by corresponding space-filling models.

Thus, on the basis of the isomerism of α - and β -endosulfan, a difference is expected to exist between the OH rate constants for the two isomers, but this cannot be estimated at present.

Literature

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