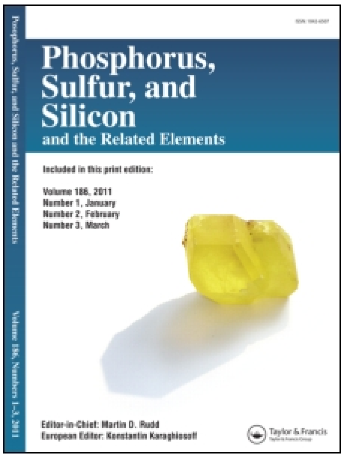

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KINETICS AND MECHANISM OF THE THERMOLYSIS OF SULFOXIDES

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KINETICS AND MECHANISM OF THE THERMOLYSIS OF SULFOXIDES

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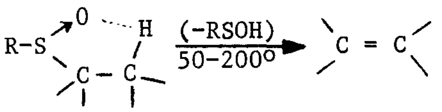
The thermolysis of sulfoxides possessing β-hydrogen atoms is a versatile and mild method to prepare olefins. The reaction is generally accepted to proceed via a concerted mechanism. Accordingly, solvent effects are not large, and appear to be associated with the initial states. The reverse process has been documented for R = t-Bu; MeSOH or PhSOH can also be employed.



$\Delta H^{\neq} = 100 - 125$ kJ/mol
$\Delta S^{\neq} = 0 \pm 40$ J/mol.°K

Compared with acetate or alkylhalide pyrolytic eliminations, little is known about structural effects. Our data show that rates of elimination from alkylsulfoxides may strongly depend on the degree of steric hindrance in the moiety containing β-hydrogen. Both initial state and transition state effects are operative here.

Regiospecificity can sometimes be very high: thermolysis of $CH_3S(O)C(CH_3)_2$-$CH(CH_3)_2$ leads to 98% 1-alkene rather than the statistical value of 86%. Studies on the temperature dependent kinetic (β) H-D isotope effect point to tunnelling in elimination from "crowded" substrates. Nonlinear Arrhenius plots are also observed.

The effect of polar substituents is even larger. Ph-$S(O)$-CH_2-CH_2-$COOCH_3$ reacts ca 10^3 times as fast as Ph-$S(O)$-$CH(CH_3)_2$, clearly by creating a favorable transition state.

Remarkably, α-$COOCH_3$— as in Ph-$S(O)$-$CH(CH_3)COOCH_3$— has a comparable accelerating effect. Ph-$S(O)$-$CH(COOCH_3)$-CH_2-$COOCH_3$ even shows $k_{rel} = 10^5 (100^\circ \text{ C})$. Electron attracting groups Z in ZPh-S(O)R, such as Z = m-NO_2 also lead to increased rates (positive Hammett rho-values throughout). These effects are due to initial state destabilisation; sulfoxide sulfur carries a markedly positive charge, which will be counteracted by neighboring electron attracting groups. Going to the transition state, this positive charge on S largely vanishes.

Initial state, transition state and final state effects (kinetics ans thermodynamics) are discussed on the basis of overall E-RC diagrams.