Kinetics of the Electrocyclic Ring Opening of α-Cyano-*cis*- and -*trans*-stilbene Oxides

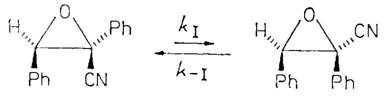
By Volker Markowski and Rolf Huisgen*

(*Institut für Organische Chemie der Universität München, Karlstrasse* 23, 8000 *München* 2, *Germany*)

Summary Kinetic studies establish the presence of high-energy intermediates (carbonyl ylides), which are formed by electrocyclic ring opening of the title compounds and which undergo 1,3-dipolar cycloadditions.

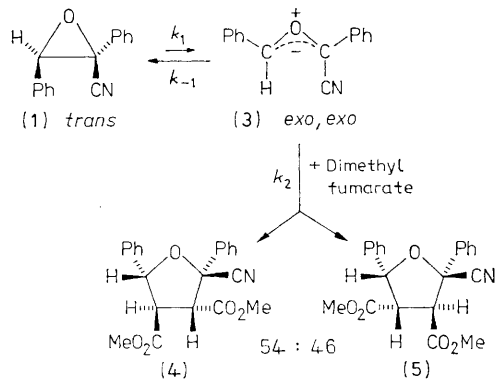
α-Cyano-*cis*- and -*trans*-stilbene oxides served as models to establish the preference for thermal conrotation[1] and photochemical disrotation[2] in the electrocyclic formation of carbonyl ylides from oxirans, thus conforming with the Woodward–Hoffmann prediction[3] for cyclopropyl anion → allyl anion conversion. We now report kinetic results which give insight into the energy profile of the four-component system consisting of *cis,trans* isomeric oxirans and carbonyl ylides.

The condensation of α-chlorophenylacetonitrile and benzaldehyde with potassium t-butoxide produced an 80:20 mixture of (**1**) and (**2**) in 90% yield. The separation was achieved by crystallisation from light petroleum (b.p. 30—40 °C).



(1) *trans* (2) *cis*

The rate of the overall isomerisation in *o*-dichlorobenzene was measured by n.m.r. analysis of the ring protons of (**1**) (τ 5·83) and (**2**) (5·25). Measurements at five temperatures provided the first-order rate constants $k_{\mathrm{I}} + k_{-\mathrm{I}}$ which were dissected with the help of the equilibrium concentrations, that of the *cis* isomer (**2**) amounting to 14·0% at 160·3 and 17·0% at 190·3 °C; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values amount to 33·9 kcal mol^{-1} and -6 cal K^{-1} mol^{-1} for k_{I}, and 32·9 kcal mol^{-1} and -5 cal K^{-1} mol^{-1} for $k_{-\mathrm{I}}$.



(1) *trans* (3) *exo,exo* (4) (5)

The reaction of (**1**) with dimethyl fumarate at 130 °C produces in 99% yield the tetrahydrofuran derivatives (**4**) and (**5**)[1] expected for conrotatory ring opening (**1**) → (**3**) and retention of configuration at 1,3-dipole and dipolarophile in the concerted cycloaddition.[4] Varying the excess concentrations of dimethyl fumarate in *o*-dichlorobenzene, we measured the cycloaddition rate constant k_{d}, which is of pseudo-first order, dilatometrically (volume shrinkage). The *exo,exo*-diphenyl substituted carbonyl ylide (**3**), formed with rate constant k_1, is a high-energy intermediate which is partitioned between recyclization (k_{-1}) and cycloaddition (k_2D); D is the concentration of the intercepting fumaric ester.

$$
\begin{aligned}
\mathrm{d[Adduct]}/\mathrm{d}t &= k_{\mathrm{d}}[\mathrm{Oxiran}] \\
&= k_{-1}[\mathrm{Oxiran}] \times k_2D/(k_{-1} + k_2D) \qquad (1)
\end{aligned}
$$

$$k_{\mathrm{d}} = k_1k_2D/(k_{-1} + k_2D) \qquad (2)$$

In the Figure experimental k_{d} values are plotted *vs.* D. The rate constants k_{d} are nonlinear functions of D and approach k_1 as plateau values in agreement with equation (2), when k_{-1} and k_2D are of a similar magnitude.

$$k_d = k_{-1} - (k_1/k_2) \times (k_d/D) \qquad (3)$$

Plotting k_d *vs.* k_d/D according to equation (3) produces straight lines, thus establishing that the bimolecular cycloaddition is preceded by a reversible first-order reaction of the oxiran (**1**). The intercepts are the rate constants of electrocyclic ring opening which allow us to calculate $\Delta H_1^{\ddagger} = 30{\cdot}1 \pm 1{\cdot}1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -2{\cdot}5 \pm 3$ cal K^{-1} mol^{-1}, whereas the slopes are k_{-1}/k_2. The slope at 130·3 °C suggests that six out of ten molecules of carbonyl ylide (**3**) are trapped by 0·5 M dimethyl fumarate and four recyclize to (**1**).

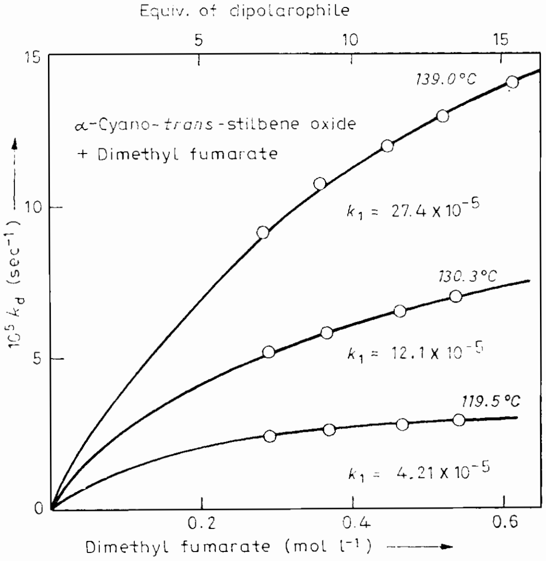
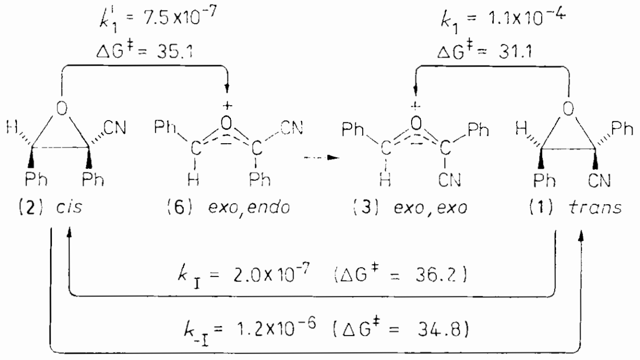


FIGURE. Dilatometric rate constants for the cycloaddition of (**1**) (0·040 mol l^{-1}) to dimethyl fumarate. The solid lines are calculated from k_1 and k_{-1}/k_2 evaluated from equation (3).

The cycloaddition of the *cis*-oxiran (**2**) and dimethyl fumarate differs fundamentally from the behaviour of (**1**): (i) The reaction is stereospecific with respect to the dipolarophile, but not for the 1,3-dipole; a mixture of 2,5-*trans*- and 2,5-*cis*-diphenyltetrahydrofuran derivatives is obtained.[1] (ii) The measured rate constant does not depend on the excess concentration D of the dipolarophile, *i.e.*, k_d is no longer a pseudo-first-order constant. In equation (3) k_{-1} becomes small compared with k'_2D and $k_d = k'_1$. (iii) The rate constant k_d of (**2**) is much smaller than that of (**1**); a $t_{\frac{1}{2}}$ value of 23 h at 148·5 °C is too slow to give precise results with dilatometry.

N.m.r. measurements of the cycloaddition rate of (**2**) and an excess of dimethyl fumarate at various temperatures afford k_{add} which are virtually identical with the overall isomerisation constant k_{-I} for (**2**) → (**1**). The formal kinetic treatment, which is given elsewhere,[5] allows only one conclusion: the barrier which has to be overcome in the electrocyclic ring opening of the *cis*-oxiran (**2**) is the highest peak in the total energy profile.



SCHEME. Rate constants in s^{-1} and activation free energies in kcal mol^{-1} at 129·6 °C.

The Scheme summarizes the kinetic evidence under the assumption that the *cis*-oxiran (**2**) undergoes only conrotatory ring opening to the *exo,endo*-diphenyl-substituted carbonyl ylide (**6**) and that the nonstereospecific portion of the reaction (**2**) + dimethyl fumarate is due to the competing rotation (**6**) → (**3**).[1] This point needs further investigation.[6]

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