EXPERIMENTAL EVIDENCE FOR A CORRELATION BETWEEN ISOSELECTIVE AND ISOKINETIC TEMPERATURES

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Summary: From isokinetic temperatures β (Figures I and II) and activation enthalpies (Table I) an isoselective temperature of 368 K is calculated for cycloaddition reactions of dihalocarbenes with alkenes. This is in excellent accord with the experimental value of 360±10 K.

Competition coefficients k_1/k_2 as well as rate coefficients k_1 and k_2 depend on the reaction temperature. Owing to this, selectivities log k_1/k_2 of molecules X_i can coincide in a narrow temperature range, the isoselective temperature $T_{i_2}^{(1)}$. Above and below T_{i_3} the selectivity order is reversed.

$$\begin{array}{c} & \begin{array}{c} & & \\ & &$$

As an example, in the competition system $BrCCl_3/CCl_4$ below 340 K the selectivity of radicals increase in the sequence $CH_3 \cdot \langle RCH_2 \cdot \langle R_2CH \cdot \langle R_3C \cdot \rangle$, and above 340 K the selectivity row is completely reversed²). In contrast to this temperature influence on selectivities an analogous inversion of reactivities at the isokinetic temperature β has been observed experimentally only in a few cases³.

Recently we have claimed that the detection of an isoselective temperature indicates the existence of isokinetic relationships and isokinetic temperatures⁴. The correlation between isoselective temperatures T_{is} and isokinetic



Figures I and II. Temperature influence on the rel. rates (log $k_3 \equiv 0$) of CF₂ and CBr₂ cycloadditions with alkenes <u>1-4</u>.

temperatures β is given by Eq.(b)⁴⁾.

$$\left[\Delta H_2^{\dagger} \right]_i = \alpha \left(\Delta H_1^{\dagger} \right)_i + \text{const.}$$
 (a)
$$T_{is} = \frac{(\alpha - 1)\beta_1 \cdot \beta_2}{\alpha \beta_1 - \beta_2}$$
 (b)

 β_1 and β_2 are the isokinetic temperatures and α is the proportionality factor between the activation enthalpies of the competitive reactions. We have now proved Eq.(b) experimentally.



In competition reactions of dihalocarbenes CX₂ with various methyl substituted alkenes <u>1-4</u> the isoselective temperatures remain constant⁵⁾. Measurements of the rel. rates between 223 and 423 K (Figures I and II) show, that the isokinetic temperatures of cycloadditions with CF₂ and CBr₂ are 620 and 230 K, respectively. From the activation enthalpies (Table I) a proportionality factor α =-0.68 results. Using the data β_1 =620 K, β_2 =230 K and α =-0.68, an isoselective temperature T_{is}=368 K can be calculated from Eq.(b). This is in excellent accord with the experimental value of 360±10 K⁵.

Table I

Rel. activation enthalpies ΔH_i^{\dagger} of the cycloaddition of dihalocarbenes CF_2 and CBr_2 with alkenes 1-4 ($\Delta H_3^{\dagger} \equiv 0.0$).

| Alkene | $\Delta H_{i}^{\dagger} [kj \cdot mol^{-1}]$ | |
|----------|--|------------------|
| | CF2 | CBr ₂ |
| 1 | 14 | -10 |
| <u>2</u> | 7.9 | -5.8 |
| <u>3</u> | ≡0.0 | ≣0.0 |
| <u>4</u> | -11 | 6.9 |

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