STERIC EFFECTS IN CARBENE CYCLOADDITIONS

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Summary: Steric effects in cycloadditions with alkenes prevent the occurence of
          a general linear free energy relationship between the reactivities of
          carbenes. Nevertheless, the isoselective temperature remains constant

In cycloaddition reactions of methylsubstituted alkenes $\underline{2}$ the selectivities
of singlet carbenes $\underline{1}$ depend only on inductive and resonance effects of substi-
tuents X and Y[1]. The absence of steric parameters indicates that the steric
repulsion between methyl groups of the alkenes and substituents X and Y of the
carbenes is negligible. Nevertheless, rate retarding effects have been observed
in cycloaddition reactions of alkenes $\underline{3}$[2] and $\underline{4}$[3] which are substituted by bul-
kier alkyl groups. A general linear free energy relationship must, therefore,
take steric effects into account. To answer the question whether a common corre
lation for reactions of singlet carbenes exists, we have measured rel. rates of
CCl_2 and CBr_2 cycloadditions with trisubstituted alkenes $\underline{5}$ using the competition
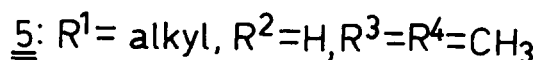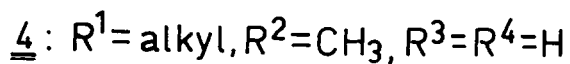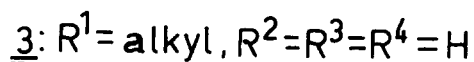technique[4] (Table I).

$$ICXY + R^1R^2C=CR^3C^4 \xrightarrow{k} R^1R^2C\!-\!CR^3R^4 \overset{CXY}{\diagup\diagdown}$$

$$\underline{\underline{1}} \qquad \underline{\underline{2}}\text{-}\underline{\underline{5}}$$

$\underline{\underline{2}}$: $R^1, R^2, R^3, R^4 = CH_3, H$ $\underline{\underline{3}}$: $R^1 = $ alkyl, $R^2 = R^3 = R^4 = H$

$\underline{\underline{4}}$: $R^1 = $ alkyl, $R^2 = CH_3, R^3 = R^4 = H$ $\underline{\underline{5}}$: $R^1 = $ alkyl, $R^2 = H, R^3 = R^4 = CH_3$
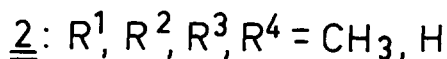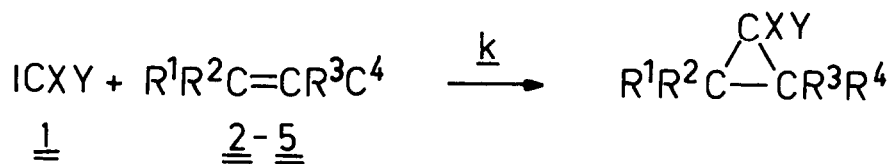
Table I

Rel. rates $\underline{k}_{CCl_2}$ and $\underline{k}_{CBr_2}$ of carbenes CCl_2 and

CBr_2 in cycloadditions with alkenes $\underline{3}$-$\underline{5}$ at $25°C$.

Substituent of the alkenes R	$\underline{k}_{CCl_2}$ Cycloadditions with alkenes			$\underline{k}_{CBr_2}$ Cycloadditions with alkenes		
	$\underline{3}$[2]	$\underline{4}$[3]	$\underline{5}$	$\underline{3}$[2]	$\underline{4}$[3]	$\underline{5}$
$\underline{a}$:CH_3	12	320	$\equiv 1000$		500	$\equiv 1000$
$\underline{b}$:C_2H_5	9.1	210		68	480	
$\underline{c}$:i-C_3H_7	4.4	77	280	30	160	350
$\underline{d}$:$CH(C_2H_5)_2$		29			60	
$\underline{e}$:$C(CH_3)_3$	0.47	14	110	2.5	38	185

A plot of the rel. rates (Table I) in a log $\underline{k}_{CBr_2}$/log $\underline{k}_{CCl_2}$-diagram shows that the reactivities of CBr_2 and CCl_2 cannot be correlated with each other. Instead of one straight line, each of the alkenes $\underline{3}$-$\underline{5}$ gives a linear free energy relationship by itself (Figure I). The slopes vary from 1.1 via 0.86 to 0.73 for reactions of monoalkylated alkenes $\underline{3}$ via dialkylated alkenes $\underline{4}$ to trialkylat-ed alkenes $\underline{5}$. This is in accord with the reactivity-selectivity principle[5] because the decrease of the selectivity (log $\underline{k}_{CBr_2}$/$\underline{k}_{CCl_2}$) parallels the increase of the reactivity (log $\underline{k}_{CBr_2}$ and log $\underline{k}_{CCl_2}$) of the alkenes (Table I).

Using only methylsubstituted alkenes (Skell-Moss line) the proportionality factor is 0.65[1]. It is, therefore, obvious that no common linear correlation exists between the reactivities of CBr_2 and CCl_2 if the number and the bulkiness of the alkyl groups at the alkenes are changed. This does not necessarily ex-clude a general relationship between selectivities log ($\underline{k}_{CXY}$/$\underline{k}_{CCl_2}$) and substi-tuent parameters of carbenes and alkenes. But such a correlation must follow the condition of a constant isoselective temperature T_{is}[5] which is $90±10°C$ for the Skell-Moss equation[6]. An extension to a relationship that also in-cludes steric substituent effects is, therefore, possible only as long as T_{is} remains at $90±10°C$. We have carried out experiments with alkene $\underline{4c}$ ($R=i$-C_3H_7) which deviates from the Skell-Moss relationship. Measurements in the competi-tion system $\underline{4a}$/$\underline{4c}$ between -20 and $100°C$ show that the selectivity lines of CF_2[7],

CCl_2 and CBr_2 cross also between 80 and 100°C (Figure 2). With this observation of a constant isoselective temperature one requirement of a common correlation of the selectivities log $(\underline{k}_{CXY}/\underline{k}_{CCl_2})$ with polar and steric substituent effects is fulfilled. To elucidate the detailed relationship experiments with further carbenes will be performed.
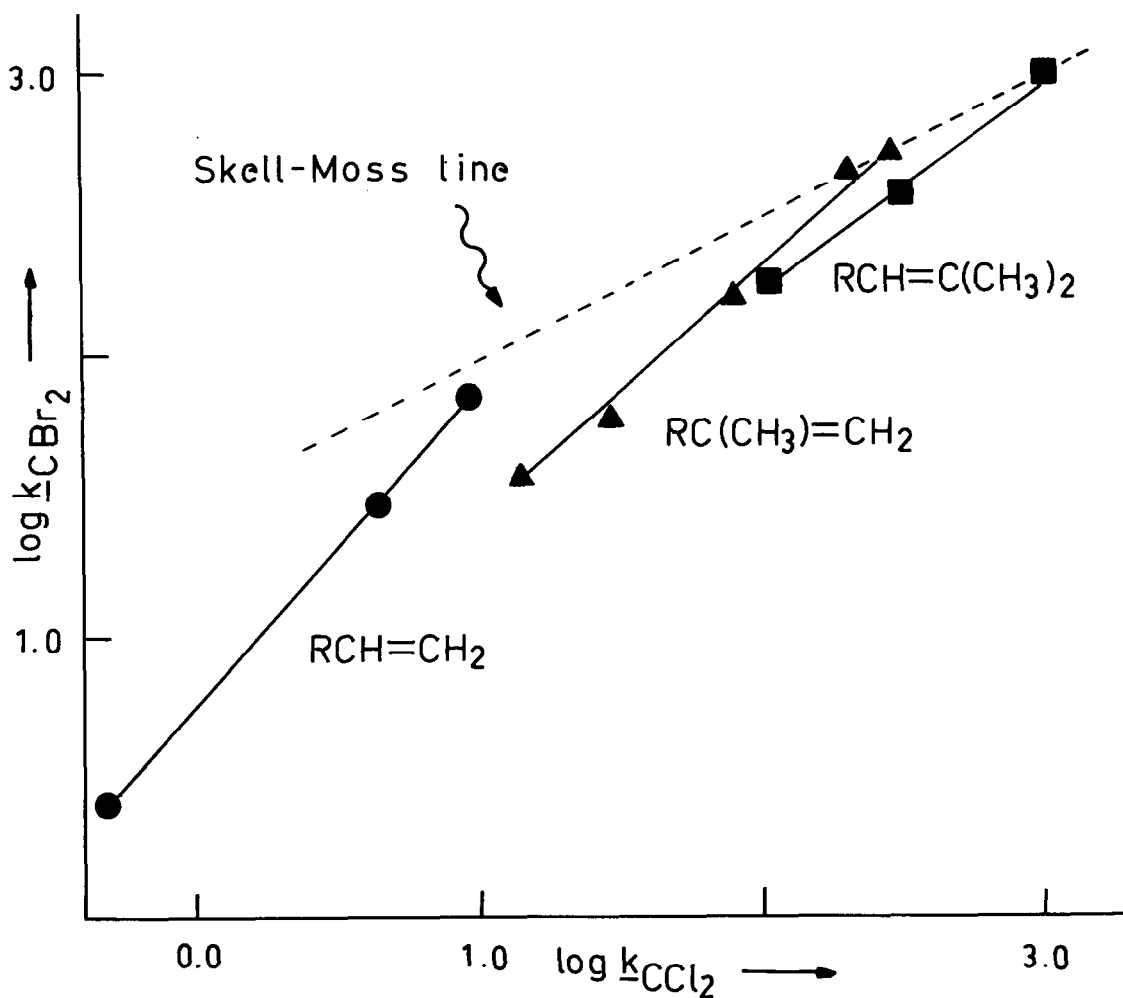

Figure I: Correlations between the rel. reactivities of CBr_2 and CCl_2 in cycloadditions with alkenes $\underline{3}$-$\underline{5}$.
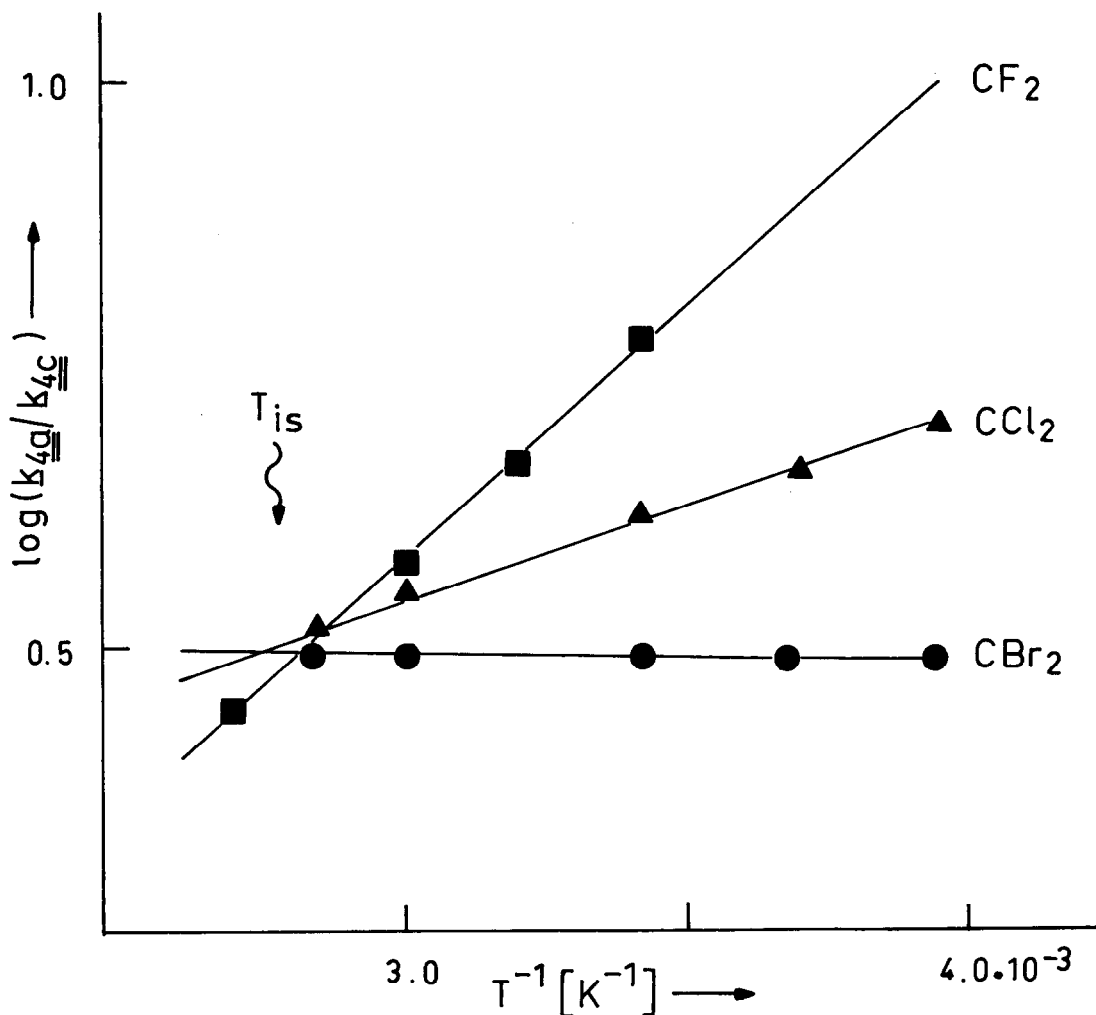
Figure II: Temperature effect on the selectivity of carbenes in the competition System 4a/4c.

References and Notes

1) R.A. Moss, Acc. Chem. Res. 13, 58 (1980).

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7) The carbenes CF_2 were generated using the method of D.J. Burton and D.G. Nase, J. Am. Chem. Soc. 95, 8467 (1973). Detailed procedure: C.W. Jefford, J. Mareda, J.C.E. Gehret, T. Kabengele, W.D. Graham and U. Burger, J. Am. Chem. Soc. 89, 2585 (1976).