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TEMPERATURE DEPENDENCE OF POLAR AND STERIC EFFECTS IN CCl_2 CYCLOADDITIONS

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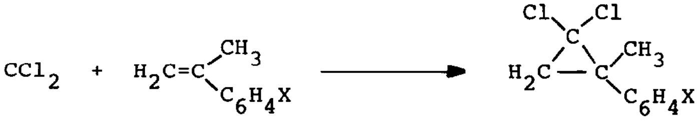
Summary: In cycloadditions of CCl_2 activation enthalpies increase with bulky substituents at the alkenes (Table I, Figure II), whereas by polar groups only activation entropies are changed.

In cycloadditions of CCl_2 with several alkylated alkenes rel. rates of the reactions do not depend on the temperature1). Therefore, by variation of methyl and n-alkyl substituents mainly the activation entropies are influenced1). This is in contrast to cycloadditions of the other mono- or dihalogenated carbenes in which the temperature plays an important role: a) Selectivities of CF_2 decrease and of CBr_2 increase by rising the temperature in cycloadditions with methylated alkenes1,2), b) with methyl and dimethyl butene C_6H_5CCl reacts slower at higher than at lower temperatures3), and c) the row of selectivities2,4) and reactivities5) of several dihalocarbenes reverses by changing the temperature.

To gain closer insight into the properties of CCl_2, competition experiments have been carried out with alkenes 1 and 2. By variation of substituents X in styrenes 1 only polar effects are altered, whereas increasing the bulkiness of alkyl groups R in alkenes 2 steric interactions can be measured.



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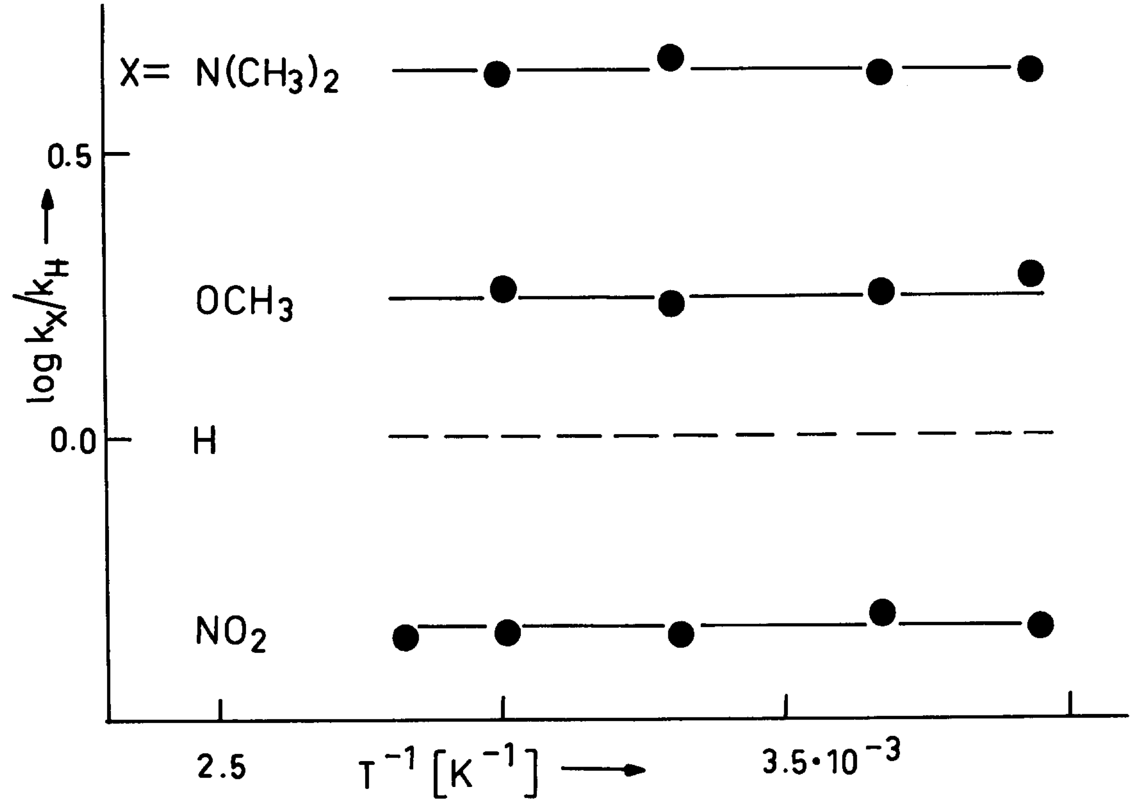
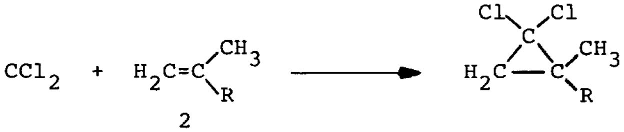


Figure I. Temperature effect on the rel. rates of CCl_2 cycloadditions to para substituted styrenes 1.

In accord with literature data[6] electron donating substituents ($X=p\text{-}N(CH_3)_2$, $p\text{-}OCH_3$) raise and electron withdrawing substituents ($X=p\text{-}NO_2$) reduce the rate of CCl_2 cycloadditions with alkenes 1. But the straight lines with zero slopes show that these substituent effects remain constant between 253 and 353 K (Figure I). On the contrary, cycloadditions of CCl_2 with alkenes 2 depend on the reaction temperature. At 253 K a t-butyl substituted alkene 2 ($R=C(CH_3)_3$) reacts 56 times slower than isobutene ($R=CH_3$). At 353 K this substituent difference is reduced to a factor of only 15 (Table I). Moreover, the slopes of the Eyring lines become more negative (Figure II) and the activation enthalpies more positive (Table I) the bulkier the groups R in alkenes 2 are.



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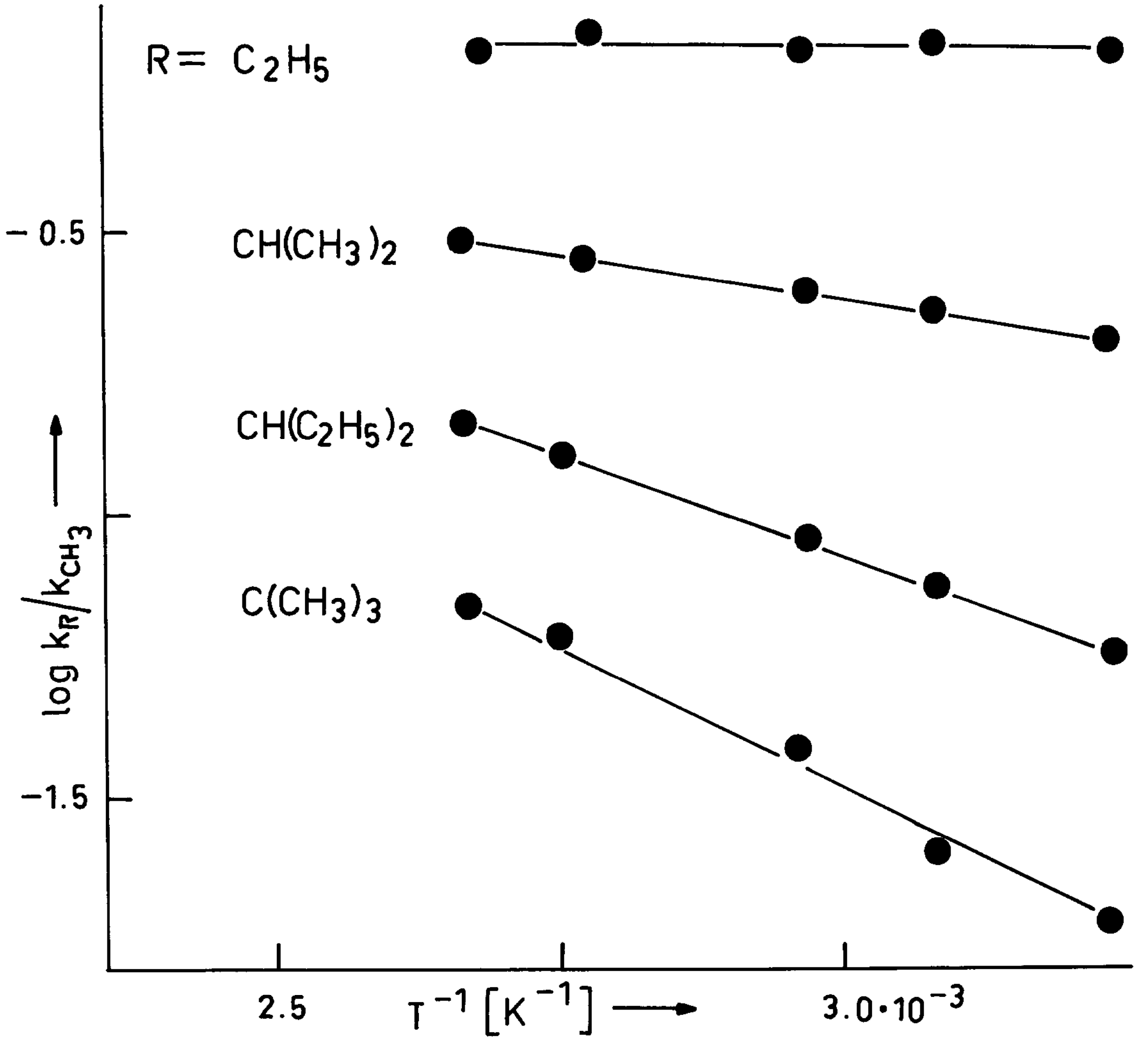

Figure II. Temperature effect on the rel. rates of CCl_2 cycloadditions to alkenes 2.

These experiments show the complete different influence of polar and steric interactions in CCl_2 cycloadditions. Increase of rate with electron releasing substituents is an entropy effect and does not depend on the reaction temperature. On the other hand, activation enthalpies are controlled by steric effects The decrease of rate caused by bulky groups, therefore, depends on the reaction temperature.

Table I

Rel. rates and activation parameters in cycloadditions of CCl_2 with alkenes 2.

	$10^2 \cdot k_{rel}$		$\Delta H^\ddagger$	$\Delta S^\ddagger$
R	253 K	353 K	$[kJ \cdot mol^{-1}]$	$[J \cdot K^{-1} \cdot mol^{-1}]$
CH_3	≡100	≡100	≡0.0	≡0.0
C_2H_5	67	64	0.0	-3.8
$CH(CH_3)_2$	19	30	3.1	-0.9
$CH(C_2H_5)_2$	5.6	15	7.2	4.5
$C(CH_3)_3$	1.8	6.5	9.9	6.1

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