Selectivity of Dihalocarbenes in Cycloaddition Reactions

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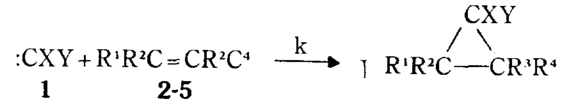
In cycloaddition reactions of methylsubstituted alkenes **2**, the selectivities of singlet carbenes **1** depend on inductive and resonance effects of substituents X and Y[1]. The absence of steric parameters indicates that the steric repulsion bentween methyl groups of the alkenes and substituents X and Y of the carbenes is negligible. Nevertheless, rate retarding effects have been observed in the cycloaddition reactions of alkenes **3**[2] and **4**[3] which contain bulkier alkyl groups. A general linear free energy relationship, therefore, may involve steric interaction. To answer the question whether a common correlation for the reactions of singlet carbenes exists, we have measured relative rates of CCl_2 and CBr_2 cycloadditions with the alkenes **3-5** using the competition technique [4] (Table 1).



$$\underset{\mathbf{1}}{:CXY} + \underset{\mathbf{2\text{-}5}}{R^1R^2C=CR^2C^4} \xrightarrow{k} R^1R^2C\overset{CXY}{\text{—}}CR^3R^4$$

2: R^1, R^2, R^3, $R^4 = CH_3$, H
3: R^1 = alkyl, $R^2 = R^3 = R^4 = H$
4: R^1 = alkyl, $R^2 = CH_3$, $R^3 = R^4 = H$
5: R^1 = alkyl, $R^2 = H$, $R^3 = R^4 = CH_3$

Table 1. Relative Rates k_{CCl_2} and k_{CBr_2} of Carbenes CCl_2 and CBr_2 in Cycloadditions with Alkenes 3-5 at 25°C

Substituent of the alkenes R	k_{CCl_2} Cycloadditions with alkenes			k_{CBr_2} Cycloadditions with alkenes		
	3[2]	**4**[1]	**5**	**3**[2]	**4**[3]	**5**
a:CH_3	12	320	1000		500	1000
b:C_2H_5	9.1	210		68	480	
c:i-C_3H_7	4.4	77	280	30	160	350
d:$CH(C_2H_5)_2$		29			60	
c:$C(CH_3)_3$	0.47	14	110	2.5	38	185

Plotting log k_{CBr_2} *vs* log k_{CCl_2} shows that the reactivities of CBr_2 and CCl_2 cannot be correlated with each other (Refer to Table 1). Instead of a straight line, each of the alkenes **3-5** gives a linear free energy relationship by itself (Figure 1). The slopes vary from 1.1 *via* 0.86 to 0.73 for the reactions of monoalkylated alkenes **3** *via* dialkylated alkenes **4** to trialkylated alkenes **5**. This is in accord with the reactivity-selectivity principle[5] because the decrease in the selectivity (log k_{CBr_2}/k_{CCl_2}) parallels the increase in the reactivity (log k_{CBr_2} and log k_{CCl_2}) of the alkenes.

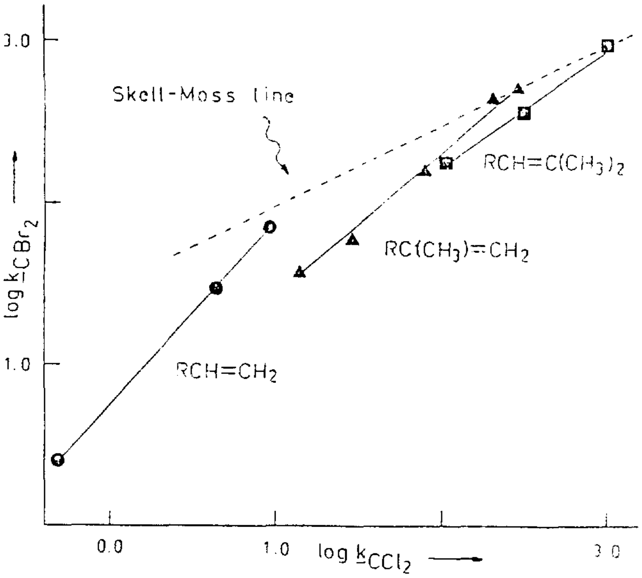


Figure 1. Correlations between the relative reactivities of CBr_2 and CCl_2 in cycloadditions with alkenes **3-5**.

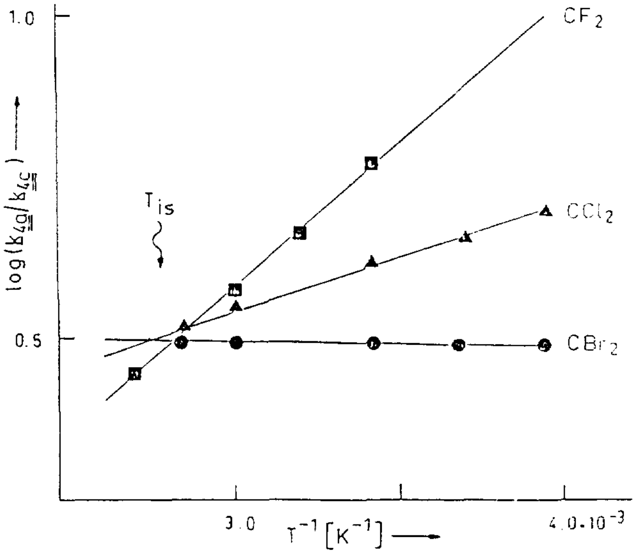


Figure 2. Temperature effect on the selectivity of carbenes in the competition system **4a**/**4c**.

With the methylsubstituted alkenes, the Skell-Moss line gives the proportionality factor of 0.65[1]. It is, thus, 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 different. This may not however necessarily exclude a general relationship between selectivities log (k_{CXY}/k_{CCl_2}) and substituent parameters of carbenes and alkenes. Such a correlation should follow the condition of a constant isoselective temperature T_{is}[5] which is 90±10°C for the Skell -Moss equation.[6] When T_{is} remains in the range of 90±10°C, substituent's stfric effect could be incorporated into the relationship. We have carried out experiments with alkene *4c* (R = i-C_3H_7) which deviates from the Skell-Moss relationship. Measurements in the competition system *4a*/*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). When increasing temperature the selectivity of CF_2 decrease, and that of CBr_2 increase, with the result that at approximately 90°C all the dihalocarbenes show the *identical* selectivity indicating isoselective temperature is approximately 90°C. Above this temperature, inverse selectivity is obeyed *i.e.* CF_2 becomes less selective and CBr_2 more selective.[8] The constant isoselective temperature may satisfy the requirement that the polar and the steric effect are to be equally well correlated with the selectivites log (k_{CXY}/k_{CCl_2}). Further work is in progress.

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References and Notes

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