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ABSOLUTE RATE CONSTANTS FOR THE ADDITIONS OF HALOPHENYLCARBENES TO ALKENES; A REACTIVITY-SELECTIVITY RELATION

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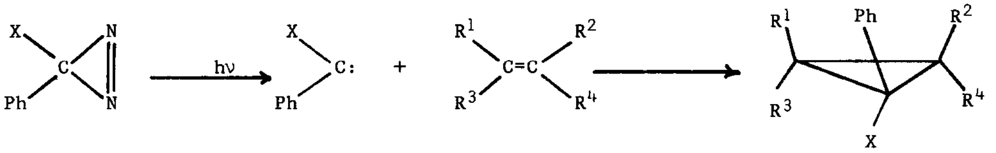
Summary. The absolute rate constants determined for the additions of FCPh, ClCPh, and BrCPh to $Me_2C{=}CMe_2$, $Me_2C{=}CHMe$, trans-MeCH=CHEt, and n-$BuCH{=}CH_2$ appear to follow a reactivity/selectivity pattern of the "normal" (inverse) type.

Much has been learned about the reactivity and selectivity of carbenes from studies of the relative rates of their cycloadditions to various alkenes.[1] Now, however, nanosecond flash photolytic techniques permit the direct measurement of absolute rate constants and activation parameters for carbene cycloadditions. We have previously applied the new methods to the addition reactions of ClCPh with alkenes,[2] and have obtained Hammett correlations for the additions of a series of p-X-PhCCl.[3] Here, we report kinetic data which constitute the first examples, obtained by direct measurements, of the dependence of carbenic reactivity on substituent variation at the carbenic carbon. The new results are important because they provide clear evidence for a "normal" reactivity/selectivity correlation in carbene/alkene addition reactions. Although such a relationship has long been assumed,[1] its general occurrence is controversial[4] and it was not observable in our Hammett study.[3]

Halophenylcarbenes 2a - 2c were generated by steady state photolysis (λ>300 nm) or flash photolysis (λ_{ex} = 351 nm) of 3-halo-3-phenyldiazirines 1a - 1c in alkene or alkene/isooctane solutions; eq. (1). Bromo and chlorodiazirines 1b and 1c were prepared by hypobromite or hypochlorite oxidations of benzamidine,[5] whereas fluorophenyldiazirine 2a was obtained by the action of molten n-$Bu_4N^+F^-$ (containing 0.1 equiv. of H_2O) on neat 1c at 25°C.[6] Appropriate cyclopropanes 4 were isolated from steady state photolyses of diazirines 1 in alkenes (3), and were identified by standard techniques.[2,7-10]



1 2 3 4 (1)

a, X=F
b, X=Cl
c, X=Br

a, X=F
b, X=Cl
c, X=Br

a, $R^1=R^2=R^3=R^4=Me$
b, $R^1=R^2=R^3=Me$, $R^4=H$
c, $R^1=Me$, $R^4=Et$, $R^2=R^3=H$
d, $R^1=$*n*-Bu, $R^2=R^3=R^4=H$

Flash photolytic studies were carried out in accord with procedures developed for ClCPh.[2] Each carbene was first photolytically generated in a 3-methylpentane matrix at 77 K and its uv spectrum was determined. These spectra were compared with point-by-point transient spectra of the same carbene generated by laser flash photolysis in aerated isooctane or benzene solutions at 23°C. Good agreement was obtained: λ_{max} values (77 K, 23°C) in nm were BrCPh, 328, 330 (isooctane); ClCPh, 307, 310 (benzene); FCPh, 270 <300 (isooctane).[11] The spectra are seen to be blue-shifted as one proceeds from BrCPh to ClCPh to FCPh. The order is that expected for the differing mix of inductive and mesomeric effects of the halogens.[12] The effect is particularly pronounced as one proceeds from ClCPh to FCPh.

The transient absorptions of laser flash generated carbenes 2 in isooctane were quenched upon addition of alkenes 3a - 3d. In the presence of sufficiently high concentrations of quencher, the decay of the transient absorptions was found to be pseudo-first-order. The slopes of the linear correlations of the decay rate constants versus alkene concentrations provided bimolecular rate constants (Table 1) for the reactions of carbenes 2 with alkenes 3.[12a]

As deduced from the stereospecificity of their additions to *cis*- and *trans*-butenes, carbenes 2a - 2c react with simple alkenes as singlets.[7,8,13] The overall span of the rate constants (Table 1) is more than two orders of magnitude; the ratio of the largest [(2c) + (3a)] to the smallest [(2a) + (3d)] rate constant is ~400. With each alkene, the XCPh absolute *reactivity* order is Br > Cl > F, which is the inverse of the carbene stability order based on anticipated halogen lone pair resonance stabilization of an adjacent, vacant, singlet carbene 2p orbital.[1] Moreover, as measured by the "spread" or ratio of the largest

Table 1. Absolute rate constants for additions of XCPh to alkenes[a]

Alkene	Carbene FCPh[b]	 ClCPh[c]	 BrCPh[b]
$Me_2C{=}CMe_2$	1.6×10^8	2.8×10^8	3.8×10^8
$Me_2C{=}CHMe$	5.3×10^7	1.3×10^8	1.8×10^8
trans-MeCH=CHEt	2.4×10^6	5.5×10^6	1.2×10^7
_n_-BuCH=CH_2	0.93×10^6	2.2×10^6	4.0×10^6
$\underline{m}_{CXY}$[d]	0.89	0.83	0.70
"spread"[e]	172	127	95

[a] Rate constants are in L/mol-sec and were determined in alkene/isooctane solution at 23°C by laser flash photolysis. Reproducibilities are <±10%. See text and ref. 2. [b] This work. [c] From ref. 3. [d] Carbene selectivity index determined at 25°C by relative reactivity studies; scale, $\underline{m}_{CCl_2}$ = 1.00. See ref. 1, first citation. [e] Rate constant ratio for additions to $Me_2C{=}CMe_2$ vs. _n_-BuCH=CH_2.

($Me_2C{=}CMe_2$) to smallest (BuCH=CH_2) rate constants, the <u>selectivities</u> of the carbenes over the common set of alkenes also follow the inverse order, FCPh > ClCPh > BrCPh. This order is identical to that of the carbene selectivity indices ($\underline{m}_{CXY}$, see Table 1) derived from comparative relative reactivity studies of XCPh and CCl_2 on a scale where $\underline{m}_{CCl_2}$ = 1.00.[1]

The comparison of absolute carbene/alkene rate constants with carbene/alkene discrimination (selectivity) (Table 1) thus provides direct evidence for an inverse relationship of absolute reactivity and selectivity or a reactivity/selectivity correlation of the "normal" type.[4] Although the significance and interpretation of such relationships, particularly in solvolytic reactions, remain controversial,[4] their occurrence in carbene/alkene cycloadditions is expected on theoretical grounds and should be "normal" for halocarbenes.[14] In this context, it is of particular interest to note that the reactions of <u>halocarbynes</u> (CF, CCl, CBr) with alkenes afford rate constant/carbyne/alkene data similar to our carbene data.[15] Thus, with any given alkene, CF is the least reactive and CBr the most reactive carbyne, whereas CF is more selective (greater "spread") than CBr over the available set of alkenes.[15]

Activation parameters for the additions of 1a and 1b to 3a and 3d have also been determined, and closely resemble the reported values for the additions of 2b to these alkenes.[2] These parameters and their interpretation will be discussed at length in our full report.[16]

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