ABSOLUTE RATE CONSTANTS FOR THE ADDITIONS OF HALOPHENYL CARBENES
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 Me₂C=CMe₂, Me₂C=CHMe, trans-MeCH=CHEt, and n-BuCH=CH₂ 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 controversial⁴ 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 (λₜₐₙ = 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-Bu₄N⁺F⁻ (containing 0.1 equiv. of H₂O) 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
Flash photolytic studies were carried out in accord with procedures developed for ClCPh. 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). 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. 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. As deduced from the stereospecificity of their additions to cis- and trans-butanes, carbenes 2a - 2c react with simple alkenes as singlets. 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. Moreover, as measured by the "spread" or ratio of the largest...
Table 1. Absolute rate constants for additions of XCPH to alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>FCPH (^{b})</th>
<th>ClCPH (^{c})</th>
<th>BrCPH (^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(_2)C=CMe(_2)</td>
<td>1.6 x 10(^8)</td>
<td>2.8 x 10(^8)</td>
<td>3.8 x 10(^8)</td>
</tr>
<tr>
<td>Me(_2)C=CHMe</td>
<td>5.3 x 10(^7)</td>
<td>1.3 x 10(^8)</td>
<td>1.8 x 10(^8)</td>
</tr>
<tr>
<td>trans-MeCH=CHEt</td>
<td>2.4 x 10(^6)</td>
<td>5.5 x 10(^6)</td>
<td>1.2 x 10(^7)</td>
</tr>
<tr>
<td>n-BuCH=CH(_2)</td>
<td>0.93 x 10(^6)</td>
<td>2.2 x 10(^6)</td>
<td>4.0 x 10(^6)</td>
</tr>
<tr>
<td>m-XY (^{d})</td>
<td>0.89</td>
<td>0.83</td>
<td>0.70</td>
</tr>
<tr>
<td>Spread (^{e})</td>
<td>172</td>
<td>127</td>
<td>95</td>
</tr>
</tbody>
</table>

\(^{a}\) Rate constants are in L/mol-sec and were determined in alkene/isooctane solution at 23°C by laser flash photolysis. Reproducibilities are <\(\pm\)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, \(m_{CCl\(_2\)} = 1.00\). See ref. 1, first citation. \(^{e}\) Rate constant ratio for additions to Me\(_2\)C=CMe\(_2\) vs. n-BuCH=CH\(_2\).
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. These parameters and their interpretation will be discussed at length in our full report.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

References and Notes


(6) R. A. Moss, D. P. Cox, and J. Terpinski, J. Am. Chem. Soc., in press. Diazirine 1a was characterized by ir, 1H, 13C, and 15N nmr, and uv spectroscopy, as well as by photolysis in alkenes to afford known FCPh adducts. Spectroscopic and preparative details for 1a are included in the manuscript in press.


(10) We thank Dr. J. Terpinski and Mr. W. Lawrynowicz for photolytic preparations of the adducts of 2c with 3c and 3d and of 2a with 3b - 3d.

(11) The transient spectrum of FCPh could not be determined accurately below 300 nm because of interfering absorption by the diazirine precursor; good agreement between low and room temperature spectra was obtained in the spectral region above 300 nm.


(12a) Available data1,13 permit comparisons of the ratios of absolute rate constants for carbene additions to Me2C=CMe2 vs. Me2C=CHMe (Table 1) with analogous classically determined1 (competition) relative rate constants. The data are (kabs ratio, krel): 3.0, 3.1 13 (FCPh); 2.2, 1.6 (CICPh); and 2.1, 1.8 (BrCPh). With reproducibilities of ±10% in kabs (±14% in the ratios), the agreements are reasonable.

(13) W. Lawrynowicz, unpublished study of 2a generated from 1a.


(16) A full paper is being prepared for a symposium-in-print issue of Tetrahedron to be devoted to carbene chemistry and published in 1984.

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