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HAMMETT ANALYSIS OF ABSOLUTE CARBENE ADDITION RATE CONSTANTS

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Summary. Absolute rate constants were determined for the additions of 5 p-X-substituted ArCCl ($X=CF_3$, Cl, H, CH_3, CH_3O) to tetramethylethylene, trimethylethylene, trans-pentene, and 1-hexene; good Hammett correlations were obtained with $\rho = +1.4 - 1.6$.

In the absence of absolute kinetic information, the alkenic selectivities of carbenes have been assessed by linear free energy comparisons of carbenic relative reactivities with standard sets of alkenes.[1] Hammett analyses generally involved substituent variation on arylalkene substrates, followed by comparisons of ρ values for several carbenes. Flash photolytic techniques now make it possible to determine absolute rate constants for additions to alkenes of carbenes previously studied only by competitive techniques.[2] We report here the first Hammett analysis of absolute rate constants for carbene/alkene additions. The results broadly support previous interpretations of carbenic reactivity, but suggest that some revisions may ultimately be required.

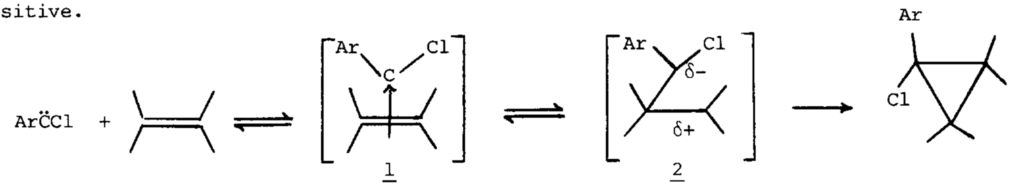
Benzamidine and 4 p-substituted derivatives (CF_3, Cl, CH_3, CH_3O) were oxidized to 3-aryl-3-chlorodiazirines.[3] Photolysis (λ>300 nm) of each diazirine in tetramethylethylene, isobutene, trans-pentene, or 1-hexene led to 20 cyclopropanes which were isolated and characterized by nmr spectroscopy and elemental analysis. Using methods and equipment described in our studies of the parent carbene, PhCCl,[2c,d] each diazirine was photolytically decomposed in 3-methylpentane matrices at 77K affording uv spectra of the corresponding arylchlorocarbenes. The spectra obtained at 77K were in good agreement with respect to shape and maximum with point-by-point transient spectra of the laser flash generated[2c,d] carbenes in aerated isooctane solution at 23°C.[4]

Laser excitation[2c,d] of isooctane solutions of the diazirines gave transient absorptions of the corresponding carbenes (ArCCl). In the presence of sufficiently high concentrations of carbene "quencher" (tetramethylethylene, trimethylethylene, trans-pentene and 1-hexene) the decay of the transient absorption followed pseudo-first order kinetics. Plots of the pseudo-first order decay constant as a function of quencher were linear under the conditions employed for analysis.[5] The bimolecular rate constants for quenching of ArCCl by each quencher were determined from the slopes of plots of decay constants versus quencher concentrations and are summarized in Table I. Hammett analyses of these results appear in Figure 1, with ρ values reported in Table I. The best correlations were obtained with σ_p^+ substituent constants,[6a] which gave correlation coefficients >0.99, significantly better than those obtained with σ_p constants.[6b]

Using standard competition methods based on cyclopropane product analysis,[1b] we determined relative reactivities of photolytically generated (λ>300 nm) ArCCl toward tetramethylethylene, isobutene, trans-pentene, and 1-hexene. Results appear in Table II, where they are normalized to $Me_2C{=}CMe_2$ and compared to k_{rel} derived from the k_{abs} data of Table I. Although the agreement in these comparisons suffices to indicate that the spectroscopically monitored kinetic species are responsible for product formation, the two sets of data are not identical within the maximal experimental error (± 20%) in all cases. Indeed, if reversible formation of a carbene/alkene intermediate (*vide infra*) is involved in these reactions,[2d] then the results of the steady state competition experiments will not match those of the time resolved experiments under the conditions of a non-negligible lifetime of the intermediate.[7]

k_{abs} for ArCCl/alkene additions varies sensibly with both aryl and alkenic substituents. From Table I, the CH_3O to CF_3 carbenic substituent change enhances k_{abs} by factors of 88-138 for the alkenes; rate constant spreads of 83-194 occur for the various carbenes in the $Me_2C{=}CMe_2/CH_2{=}CH{-}C_4H_9$ comparison. The k_{abs} ratio for the fastest (*p*-$CF_3C_6H_4CCl$ + $Me_2C{=}CMe_2$) *vs.* the slowest addition (*p*-$CH_3OC_6H_4CCl$ + $CH_2{=}CH{-}C_4H_9$) is 4 orders of magnitude. The Hammett analyses show that electron-donating (ED) substituents in ArCCl retard, whereas electron-withdrawing (EW) substituents accelerate the additions; ρ values are $\sim+1.5$ with little dependence on alkene.[8]

Qualitatively, $\rho>0$ might be interpreted to mean that ED substituted ArCCl are more stabilized than EW substituted ArCCl,[10] and therefore react more slowly with a given alkene. Recent evidence that carbene/alkene additions may proceed *via* intermediates (*e.g.*, **1** in eq. (1), a charge transfer complex) complicates the matter,[11] but rationalization of the ρ values can still be made by focussing on the intermediate. When X is EW, passage of **1** to product over "electrophilic" transition state **2** is favored because X stabilizes enhanced negative charge imposed on the carbenic carbon. Dissociation of **1** to carbene and alkene is disfavored, however, because EW substituents destabilize carbenes.[10] When X is ED, these considerations reverse. Now **2** is destabilized and the dissociation of **1** to carbene and alkene is favored. Thus, EW groups enhance product formation from **1**, but ED groups favor reversion of **1** to ArCCl, and ρ based upon the disappearance of ArCCl should be positive.



(1)

The absence of a substituent dependence on the selectivity of these ArCCl additions to alkenes is striking and unexpected.[8] Although current ideas (*e.g.*, molecular orbital calculations)[1a,10] concerning the [1+2] cycloaddition of carbenes to alkenes have not explicitly involved the concept of a reversibly formed intermediate, such an idea provides a possible basis for explaining the unusual temperature dependence of the kinetics of these reactions,[2d] the absence of altered selectivity despite a large change in reactivity, and the differences between the steady state and time resolved kinetic results. For example, if for a particular carbene/alkene system complex formation is involved in the rate determining step, a very fast reaction (high reactivity) may still be selective if the factors which determine selectivity control the passage of the intermediate to product. Furthermore, if the concentration of quencher becomes very high, as it does for a steady state competition experiment, a carbene moiety involved in a reversibly formed carbene/alkene intermediate might be "trapped" by a different alkene, thereby leading to a concentration dependent product ratio. We believe that our results provide new insight into the seemingly simple [1+2] cycloaddition and serve to encourage further theoretical and experimental investigations.

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Table I. Absolute Rate Constants for Additions of p-X-C_6H_4CCl to Alkenes[a]

Alkenes	X: CH_3O	CH_3	H[b]	Cl	CF_3	ρ[c]
$Me_2C=CMe_2$	1.4×10^{7}[d]	1.2×10^{8}	2.8×10^{8}	3.3×10^{8}	1.5×10^{9}	1.5
$Me_2C=CHMe$	7.7×10^{6}	4.9×10^{7}	1.3×10^{8}	1.8×10^{8}	6.8×10^{8}	1.4
t-MeCH=CHEt	4.4×10^{5}	1.8×10^{6}	5.5×10^{6}	7.5×10^{6}	4.9×10^{7}	1.5
$CH_2=CH$-n-C_4H_9	1.3×10^{5}[d]	6.2×10^{5}	2.2×10^{6}	2.3×10^{6}	1.8×10^{7}	1.6

[a] Rate constants are in L/mol-sec and were determined in alkene/isooctane solution at 23°C by laser flash photolytic methods; see text and refs. 2c and 2d. Reproducibilities are <± 10% unless otherwise noted. [b] These data differ slightly from those previously reported[2d] due to modifications in equipment. All data reported here were determined under identical conditions. [c] ρ values are rounded to 2 significant figures. All correlation coefficients were >0.99. For σ_p^+ constants, see ref. 6a. [d] Reproducibility is ± 15%.

Table II. Relative Reactivities for Additions of p-X-C_6H_4CCl to Alkenes[a,b]

Alkenes	X: CH_3O	CH_3	H	Cl	CF_3
$Me_2C=CMe_2$	1.00	1.00	1.00	1.00	1.00
$Me_2C=CH_2$	0.37	0.26	0.25	0.22	0.24
t-MeCH=CHEt[c]	0.038 (0.031)	0.028 (0.015)	0.028 (0.020)	0.029 (0.023)	0.033 (0.033)
$CH_2=CH$-n-C_4H_9[c]	0.017 (0.0093)	0.012 (0.0052)	0.012 (0.0079)	0.012 (0.0070)	0.012 (0.012)

[a] Relative reactivities were determined at 25°C in neat alkene mixtures. Product separation and quantitation was achieved by reversed phase hplc on a Waters C-18 RCM column, using CH_3CN or 10-15% H_2O/CH_3CN as eluents, a calibrated uv detector, and an electronic integrator. Results are generally averages of 2 or more runs and were usually determined in competition against isobutene. Reproducibilities were <± 9%, and all but 3 cases were <± 5%. Appropriate cross-checks[1b] were done. [b] Values in ( ) are calculated from the absolute rate constants of Table I. [c] Relative reactivities are based on the sum of the syn/anti cyclopropane mixture obtained with this alkene.

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(4) λ_{max} values (77K, 23°C) for ArCCl were (nm): p-CH_3O, 346, 340; p-CH_3, 317, 317; H, 307, 310 (benzene); p-Cl, 323, 320; p-CF_3, 303, 298. For solution kinetic studies, carbene absorptions were monitored at 320 nm, except for p-$CH_3OC_6H_4$CCl (330 nm).

(5) The use of kinetics to uncover unexpected aspects of the reactions of PhCCl with alcohols has recently been reported: D. Griller, M.T.H. Liu, and J.C. Scaiano, J. Am. Chem. Soc., 104, 5549 (1982).

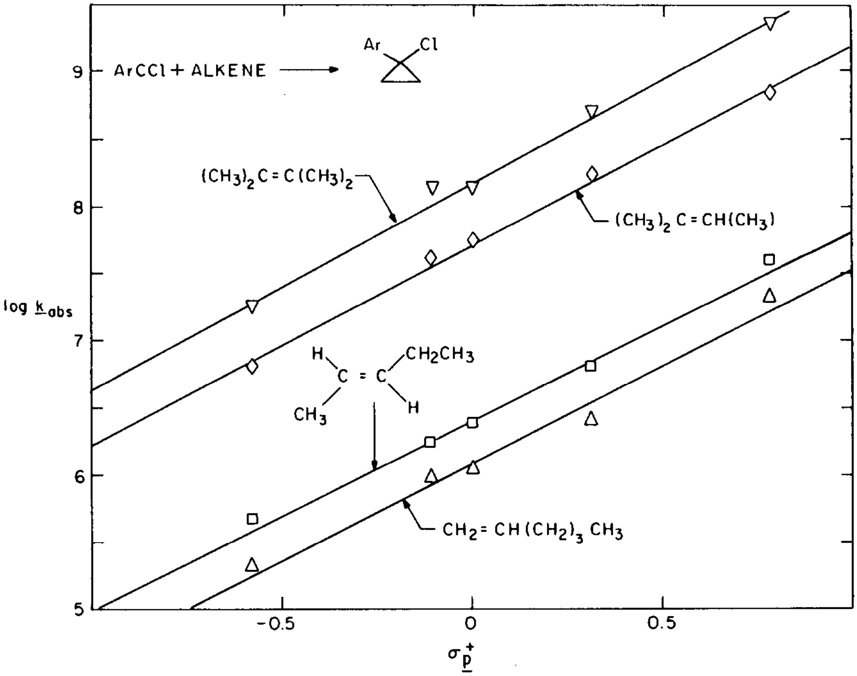

Figure 1. Logarithms of absolute rate constants (L/mol-sec) for additions of ArCCl to $Me_2C{=}CMe_2$, $Me_2C{=}CHMe$, t-MeCH=CHEt, and $CH_2{=}CH$-n-C_4H_9 vs. σ_p^+. For ArCCl substituents and ρ values, see Table I.

(6) (a) C.D. Ritchie and W.F. Sager, *Prog. Phys. Org. Chem.*, 2, 323 (1964); *cf.*, pp. 334-337. The value for σ_p^+ (CF_3) is taken from C.G. Swain and E.C. Lupton, Jr., *J. Am. Chem. Soc.*, 90, 4328 (1968). (b) J. March, "Advanced Organic Chemistry", 2nd Ed., McGraw-Hill, New York, 1977, p. 253.

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(8) Although classic electrophilic selectivity[1a,1b] is apparent with all 5 ArCCl (*i.e.*, the most highly alkylated olefins react most rapidly[9]) the carbenes are all *comparably selective* over the olefin set; the four Hammett correlations are nearly parallel. This lack of selectivity variation is also apparent from the k_{rel} data of Table II.

(9) The anticipated electrophilic behavior is also apparent in additions of PhCCl to either simple alkenes[1b] or to ring-substituted styrenes, for which ρ varies from -0.56 to -1.06 depending on temperature: *cf.*, W. Brück and H. Dürr, *Tetrahedron Lett.*, 23, 2175 (1982).

(10) Electron-donating substituents stabilize carbenes by π-type resonance interactions; *cf.*, N.G. Rondan, K.N. Houk, R.A. Moss, *J. Am. Chem. Soc.*, 102, 1770 (1980) and references therein.

(11) For additions to $Me_2C{=}CMe_2$, we find (unpublished work) that both p-CF_3 and p-CH_3O derivatives of PhCCl exhibit k_{abs} *vs.* 1/T dependencies similar to that of PhCCl itself; *i.e.*, "negative" activation energies which are kinetically consistent with the presence of an intermediate.

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