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Carbene Olefin Complexes and Carbene Philicity

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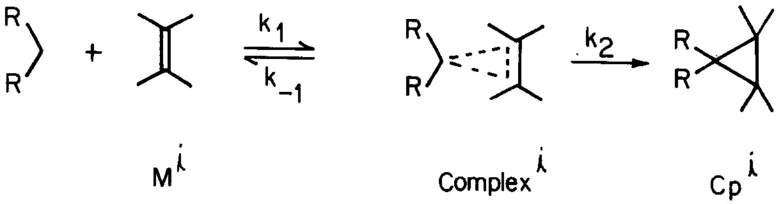
Summary: The effect of carbene-olefin complexation on the relationship between absolute rates obtained by laser flash photolysis and product ratios are considered. The conditions needed to give linear Hammett plots in the complex mechanism are detailed.

In recent years the technique of laser flash photolysis has been used to obtain absolute rate data for the reactions of carbenes with olefins in solution.[1] A key connection between laser and product analysis has been the demonstration that the relative yields of cyclopropanes derived from competitive trapping of a given carbene with a pair of olefins is the same ratio predicted by the ratio of the absolute rate constants of the carbene with the individual trapping agent. However, recent work of Moss and Turro has demonstrated that the reaction of phenylchlorocarbene is not a simple one step process, but most likely proceeds by carbene olefin complexation followed by cyclopropane formation.[2]



Moss and Turro have pointed out that in this circumstance the observed rate of carbene decay (k_{obs}) is a composite function. Thus,

$$(1)\qquad \frac{-d[R_2C]}{dt} = k_1[R_2C][M^i] - k_{-1}[\text{Complex } i] \text{ and}$$

$$(2)\qquad \frac{-d[R_2C]}{dt} = k^i_{obs}\,[R_2C][M^i] \qquad \text{where (3)} \quad k_{obs} = \frac{k_1k_2}{k_{-1} + k_2},$$

if one assumes the steady state condition for $complex^i$,

$$(4)\qquad \frac{d\ complex^i}{dt} = k_1[R_2C][M^i] - k_{-1}[complex^i] - k_2[complex^i] = 0.$$

The rate of cyclopropane formation is

$$(5)\qquad \frac{d[C_p{}^i]}{dt} = k_2[complex^{-1}] = \frac{k_1k_2}{k_{-1} + k_2}\,[R_2C][M^i] = k^i_{obs}\,[R_2C][M^i]\ .$$

In a competition experiment using M^o and M^l, the product ratio is

$$(6)\qquad \frac{C_po}{C_pl} = \frac{d[C_po]/dt}{d[c_pl]/dt} = \frac{k^o_{obs}}{k^l_{obs}}$$

Thus even when a complex mechanism is operative the product ratios will equal the ratio of absolute rate constants as long as the lifetime of the complex is very short (the steady state assumption). Some discrepancies between laser flash and product data have been noted.[2]

The philicity of various carbenes towards a standard set of olefins has been determined by Moss and coworkers.[3] The Hammett ρ values for cyclopropanation reactions of many carbenes have also been obtained.[4] If cyclopropanation occurs by complex formation, and if complex formation is fast relative to rate determining cyclopropanation, then[5]

$$(7)\qquad \frac{-d[R_2C]}{dt} = \frac{d[C_pi]}{dt} = k_2K[R_2C][M^i] \text{ where } K = \frac{[\text{complex}^i]}{[R_2C][M^i]}$$

$$\text{thus,}\qquad \log\left(\frac{k^o_{obs}}{k^o_{obs}}\right) = \log\left(\frac{K^1}{K^o}\right) + \log\left(\frac{k_2{}^1}{k_2{}^o}\right) = \sigma(\rho_K + \rho_{k_2})\ .$$

Thus the measured ρ′ value is a composite of the two values for each step of the reaction. In this mechanism then, the cyclopropane reaction will follow a linear free energy relationship, but, the absolute value of ρ′ may be smaller than the absolute value of either ρ_K or ρ_{k_2}, as these latter terms may be of opposite sign. However, if complex formation is comparable to product formation ($k_{-1} \simeq k_2$) then Equation (8) will hold,

$$(8)\quad \log\left(\frac{k^o_{obs}}{k^o_{obs}}\right) = \log\left(\frac{k^1_1k^1_2/(k^1_{-1} + k^1_2)}{k^o_1k^o_2/(k^o_{-1} + k^o_2)}\right) \qquad (9)\quad \log\left(\frac{k^1_{obs}}{k^o_{obs}}\right) = \frac{k^1_1}{k^o_1} = \sigma\rho_1$$

which cannot be further simplified, and will not necessarily obey a linear free energy relationship. Of course, if there is a change in the rate determining step in the complex mechanism, with variation of olefin, a non-linear Hammett plot will result. If complex formation is rate determining relative to fast complex collpase ($k_2 \gg k_{-1}$) then Equation (8) simplifies to (9) and a linear Hammett relationship will again hold, although the meaning of ρ has changed from that of (7).

The widespread occurrence of valid correlations of carbene reactions means that complex formation may not be a general phenomenon, or that when it does occur, complexation is much faster or much slower than the product formation step.

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