Activation Parameters for the Reaction of Phenylchloro Carbene with Pyridine,
Tri-n-butyltin Hydride, and Triethylsilane; Evidence Against the Need
to Invoke Reversibly Formed Complexes in the Reaction of
This Carbene with Olefins

by

James E. Jackson[‡*], N. Soundararajan and Matthew S. Platz[*]
Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

Michael P. Doyle   and   Michael T. H. Liu
Department of Chemistry   Department of Chemistry
Trinity University   University of Prince Edward Island
San Antonio, Texas   Charlottetown, P.E.I.

Abstract. The activation energies for reaction of phenylchloro carbene with pyridine, tri-n-butyl-tin hydride and triethylsilane are reported. The data argues against reversibly formed complexes in the reaction of this carbene with olefins.

In the last decade laser flash photolysis (LFP) has provided quantitative data on the absolute reactivity of carbenes towards typical substrates.[1] Moss, Turro, et al. have reported particularly thorough studies of the rates and mechanisms of reactions of singlet aryl halo carbenes with olefins to give cyclopropanes.[2] They have systematically varied the olefin, the halogen atom and the substitution on the aromatic ring, effectively demonstrating the electrophilic nature of this cycloaddition. One of the most intriguing results was their observation of curved Arrhenius plots which yielded apparently negative activation energies for the reaction of phenylchlorocarbene (PCC) with electron rich olefins such as tri- and tetramethylethylene (TME) at temperatures down to ~ 230 K.[2a,b] We have duplicated their study of TME reacting with PCC (Reaction 1 and Table 1), with essentially similar results.

Two explanations have been advanced to interpret these unusual observations. A negative activation energy could be the consequence of a reversibly formed carbene-olefin complex formed along the cyclopropanation reaction coordinate.[3] (Irreversibly formed complexes can not produce negative activation energies.) This was the explanation offered in the original work,[2a] and it has also been used to analyze subsequent examples of unusual kinetic behavior in carbene reactions as well.[2b,c]

An alternative interpretation has been advanced by Houk and Rondan,[4] whose calculations find no evidence for an intermediate complex and no enthalpic barrier in reaction (1). However, because $\Delta S^{\ddagger}$ is large and negative, there is a temperature-dependent free energy barrier that is solely entropic in origin. Thus, the reaction rate increases with decreasing temperature as $-T\Delta S^{\ddagger}$, and hence $\Delta G^{\ddagger}$, become smaller. Furthermore, because of the steep variation of ΔS along the reaction coordinate, the value of E_a and hence of $\Delta H^{\ddagger}$ show strong temperature dependence as reflected in the <u>curvature</u> of the Arrhenius plot.

We have recently reported that PCC reacts with pyridine (PYR, Reaction 2) and tri-n-butyltin hydride (TTH, Reaction 3) in toluene with room temperature rate constants comparable to that for TME.[5a,b] This has prompted the present study of the temperature dependence of the rate constants for reactions 2 and 3 (Table 1). For comparison, we have also examined the much less reactive substrate triethylsilane (TES, Reaction 4), and reexamined the temperature dependence of the PCC-TME reaction (Reaction 1, Table 1).

‡ Current address, Department of Chemistry, Michigan State University,
  East Lansing, Michigan 48824
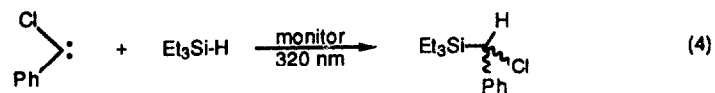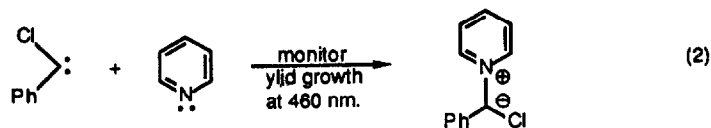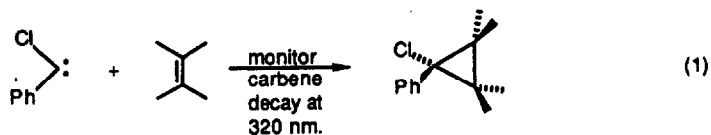
The activation energies for reactions (2) and (4) are roughly comparable to that of PCC with 1-pentene (1.34 ± 0.51, 2.76 ± 0.05, and 1.9 ± 1.0 kcal/mol, respectively). However, the activation energy for reaction (3) is -0.13 ± 0.04 kcal/mol (see Figure 1). We have confirmed Moss and Turro's report that the activation energy for reaction (1) is -1.3 kcal/mol (we find -1.28 ± 0.03 kcal/mol) in toluene in the temperature range 260-320K.[2a] The reactions of PCC with triethylsilane, pyridine and tri-n-butyl tin hydride have an isokinetic temperature near 222K although we are not sure what, if any, significance we should attribute to this phenomenum.

The magnitude of a diffusion controlled rate constant in toluene can be calculated from

$$k_{DIFF} = \frac{8RT}{3000\eta}$$

where R and T have their usual meanings and η is the viscosity in centipoise.[6] Using the known temperature dependent viscosity of toluene[7] it was possible to calculate the apparent activation energy of a diffusion controlled reaction in this solvent (E_a = 2.67 kcal/mol) in the relevant temperature regime. Thus although the activation energy for PCC with 1-pentene is positive it is still almost a kcal/mol less than that of a diffusion controlled process.

Reversibly formed intermediates in reactions (2) - (4) do not appear plausible. One can in fact view the pyridinium ylid in reaction 2 as a model for the putative carbene-olefin complex. This pyridinium ylid is long lived ($\tau_{1/2}$ > 10 μs), other pyridine ylids are in some cases isolable.[8] To our knowledge, there is no evidence that they can revert to pyridine and free carbene.

The fact that a negative activation energy for a PCC reaction can be observed where complex formation is implausible indirectly supports the Houk-Rondan model[4] of entropically controlled barriers. At the very least it suggests that such behavior is not necessarily diagnostic for complex formation.[9,10]

Table 1: Arrhenius Activation Parameters for Reactions of Phenylchlorocarbene

Compound	E_a(Kcal/mol)[a,b]	Log A[a,b]	T range
Tetramethylethylene (TME)	-1.28 ± 0.03	7.04 ± 0.02	-20 to +61
Tri-n-butyltin hydride (TTH)	-0.13 ± 0.04[c]	8.20 ± 0.03[c]	-41 to +62
Pyridine	+1.34 ± 0.51[d]	9.70 ± 0.21	-73 to +62
1-Pentene	+1.90 ± 1.0[e] 7.5 ± 1.0[e]	-20 to +20	
Triethylsilane	+2.76 ± 0.06 8.48 ± 0.43	-32 to +25	

a) Rates and hence activation parameters not corrected for solvent contraction.
b) Uncertainties reported are ± 4 SD. These uncertainties are obviously low in some cases, and reflect only random errors. c) These activation parameters were obtained from the five highest temperature points for TTH, since the lowest temperature point seems to begin a downturn. If all points are used, the results are: E_a = -0.092 ± 0.078 kcal/mol; Log A = 8.23 ± .06. d) These activation parameters were obtained from a plot of all the data points collected during this study. e) Reference 3a.

Figure 1. Arrhenius plots for the reaction of phenylchloro carbene with pyridine (PYR), trio-n-butyltin hydride (TTH) and tetramethylethylene (TME). DIFF corresponds to an Arrhenius plot of a diffusion controlled reaction in toluene (see text).
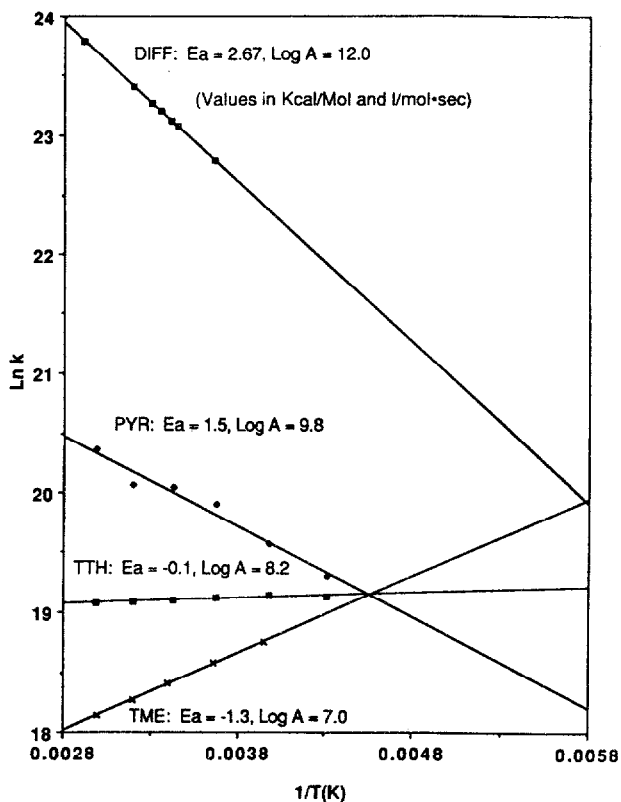
The Houk/Rondan model is based on calculations which best represent gas-phase behavior. It is not obvious that this picture can be completely transferred into solutions, even those as nonpolar as toluene or isooctane. However, the present work simply illustrates the fact that unusual Arrhenius behavior may arise even in situations where complex formation seems improbable. It thus diminishes the necessity to invoke the intermediacy of a complex in the reaction of PCC with olefins.

Acknowledgement

References

1. Scaiano, J. C. "Kinetics of Carbene Reactions" in Chemical Kinetics of Small Organic Radicals, Alfassi, Z. B., Ed.; CRC Press: Boca Raton, Florida; **1988**; 3; Ch. 13; p.73ff.

2. (a) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. Tetrahedron **1985**, 41, 1587. (b) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. J. Am. Chem. Soc. **1986**, 108, 7028. (c) Turro, N. J.; Okamoto, M.; Gould, I. R.; Moss, R. A.; Lawrynowicz, W.; Hadel, L. M. J. Am. Chem. Soc. **1987**, 109, 4973.

3. For a discussion of the properties of such a complex, see Soundararajan, N.; Jackson, J. E.; Platz, M. S.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H. J. Am. Chem. Soc. **1988**, 110, 0000 (in press), and Platz, M. S.; Tetrahedron Lett. **1983**, 24, 4763.

4. Houk, K. N.; Rondan, N. G.; Mareda, J. Tetrahedron **1985**, 41, 1555. See also Houk, K. N.; Rondan, N. G.; Mareda, J. J. Am. Chem. Soc. **1984**, 106, 4291 and 4293.

5. (a) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. J. Am. Chem. Soc. **1988**, 110, 0000 (in press). (b) Doyle, M. P.; Taunton, J.; Oon, S.-M.; Liu, M. T. H.; Soundararajan, N.; Platz, M. S.; Jackson, J. E., submitted for publication in Tetrahedron Lett.

6. Caldin, E. F.; "Fast Reactions in Solution"; John Wiley, New York, N.Y. (1964) Chapter 1.

7. "Handbook of Chemistry and Physics," Weast, R. C., ed. CRC Press, 51st edition (1970-1971) p. F-42.

8. Zugravescu, I.; Petrovanu, M. N-Ylid Chemistry; McGraw-Hill International Book Company; New York, NY; **1976.**

9. Skell, P. S.; Cholod, M. S. J. Am. Chem. Soc. **1969**, 91, 7131.

10. Giese, B.; Meister, J. Angew. Chemie Int. Ed. Engl. **1978**, 17, 595.
    Giese, B.; Lee, W.-B. Ibid **1980**, 19, 835.
    Giese, B.; Lee, W.-B. Meister, J. Liebigs Ann. Chem. **1980**, 725.
    Giese, B.; Lee, W.-B. Chem. Ber. **1981**, 114, 3306.
    Giese, B.; Lee, W.-B.; Neumann, C. Angew. Chemie Int. Ed. Engl. **1982**, 21, 310.