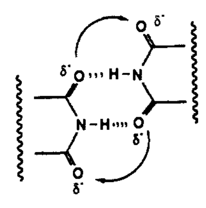
are that lactams or, more generally, amides will be better complements to peptides in the design of structures for their molecular recognition.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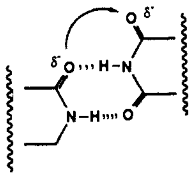
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Acknowledgment. We thank the National Institutes of Health for support and Professor W. Jorgensen for helpful discussions.

Absolute Kinetics of Dichlorocarbene in Solution[†]

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Received December 18, 1989

Dichlorocarbene is the cornerstone of singlet carbene reactivity. Moss has thoroughly characterized carbenic selectivity in cyclopropanation reactions.[1,2] The reactivity of any singlet carbene (:CXY) may be standardized by comparison of its reactivity toward a "standard" set of alkenes with that of dichlorocarbene ($:CCl_2$). Amazingly, however, the absolute kinetics of this important reactive intermediate have not been measured to date.[3] This is primarily due to the lack of a suitable photolabile precursor. Herein, we report a clean photolytic source of $:CCl_2$ and the first absolute rate constants for reaction of $:CCl_2$ with olefins in solution.

7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (**1**)[4] proves to be a suitable photochemical source of $:CCl_2$.[5,6] UV (280 nm) photolysis of 1×10^{-3} M **1** in hexane generates phenanthrene (**2**) with a quantum efficiency of 0.078[7] and essentially quantitative chemical yield. Under similar conditions, photolysis of **1** in cyclohexene yields the $:CCl_2$ adduct (**3**) in ≥90% yield. A clean photoextrusion of $:CCl_2$ is also indicated by production of **2** and **3** as the principal products[8] following 266-nm laser irradiation of 1×10^{-4} M **1** in cyclohexene. Encouraged by these results and with hope of direct optical detection of $:CCl_2$ in solution,[9] we used laser flash photolysis (LFP) to investigate the photodecomposition of **1** in cyclohexane (C_6H_{12}) (Scheme I).

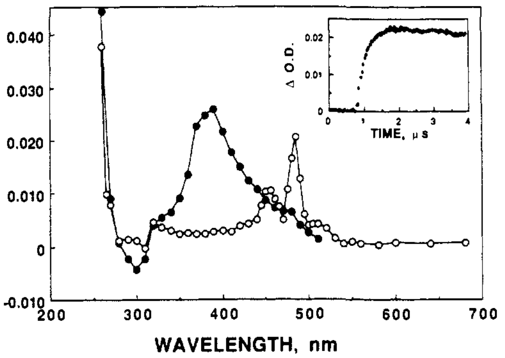

Figure 1. Transient absorption spectra observed 1.02 and 1.13 μs after 266-nm LFP of 5×10^{-5} M **1** in N_2-saturated C_6H_{12} (○) and 1×10^{-4} M **1** in air-saturated C_6H_{12} containing 5.24×10^{-4} M pyridine (●), respectively. Insert shows a representative single-exponential growth ($k_{exptl} = 4.1 \times 10^6$ s^{-1}) of pyridinium ylide **4** monitored at 400 nm.

Scheme I

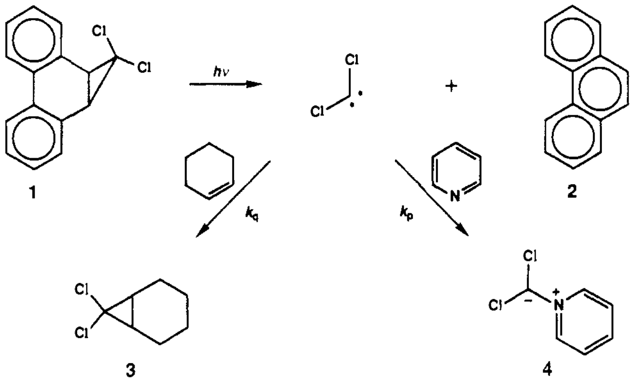

Table I. Absolute Rate Constants for Reaction of Dichlorocarbene[a] and Phenylchlorocarbene[b] with Olefins

substrate	$:CCl_2$ k,[c] M^{-1} s^{-1}	PhCCl k, M^{-1} s^{-1}
$Me_2C{=}CMe_2$	$(3.81 \pm 0.16) \times 10^9$	2.8×10^8
$MeCH{=}CMe_2$	$(2.23 \pm 0.24) \times 10^9$	1.3×10^8
trans-$MeCH{=}CHEt$	$(6.31 \pm 0.63) \times 10^7$	5.5×10^6
c-C_6H_{10}	$(3.50 \pm 0.12) \times 10^7$	
$CH_2{=}CH$-*n*-C_4H_9	$(1.08 \pm 0.05) \times 10^7$	2.2×10^6

[a] This work, measured by monitoring the competitive kinetics of formation of pyridinium ylide **4** at 400 nm in cyclohexane at 21 °C; see text. [b] Data taken from ref 23. Rates were measured in isooctane. [c] Errors represent ±2 standard deviations.

Unfortunately, LFP (266 nm, ~8 mJ)[10] of 5×10^{-5} M **1** in N_2-saturated C_6H_{12} does *not* result in an absorption band in the 250–750-nm regime that can be attributed to singlet $:CCl_2$.[11] Instead, the well-known triplet–triplet absorption spectrum of phenanthrene (λ_{max} = 485 nm, shoulder = 460 nm)[12] is observed

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[†] This paper is dedicated to Professor Wolfgang Kirmse on the occasion of his 60th birthday.

(1) For a review of carbene selectivity, see: Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58–64.

(2) See also: (a) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, Chapter 3. (b) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, Chapter 3. (c) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley-Interscience: New York, 1975; Vol. II. (d) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley-Interscience: New York, 1973; Vol. I. See, in particular: Moss, R. A. *Ibid.* Chapter 2. (e) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (f) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

(3) For reports of gas-phase fluorescence quenching rates of $:CCl_2$, see: Tiee, J. J.; Wampler, F. B.; Rice, W. W., Jr. *Chem. Phys. Lett.* **1980**, *73*, 519–521. Huie, R. E.; Long, N. J. T.; Thrush, B. A. *Ibid.* **1977**, *51*, 197–200.

(4) The synthesis of **1** has been previously described. Joshi, G. C.; Singh, N.; Pande, L. M. *Synthesis* **1972**, 317.

(5) Photolysis of the parent hydrocarbon, 9,10-dihydro-9,10-methanophenanthrene, generates products identical with those from photolysis of diazomethane. Richardson, D. B.; Durrett, L. R.; Martin, J. M., Jr.; Putman, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763–2765.

(6) For a review of carbene generation by photochemical cycloelimination, see: Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *10*, 537–547.

(7) Determined by potassium ferrioxalate actinometry.

(8) Determined by comparison with authentic samples of **2** and **3** by GC analysis.

(9) There has been a report of a weak absorption spectrum, ranging from 440 to 560 nm, that was attributed to $:CCl_2$, formed by the reaction of carbon atoms with molecular chlorine in Ar and N_2 matrices at 14 K. Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1967**, *47*, 703–707.

(10) The LFP equipment is described elsewhere. Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

(11) Reactivity is not expected from the lowest triplet $:CCl_2$, which is predicted to be 13.5 kcal/mol above ground-state singlet $:CCl_2$. Bauschlicher, C. W., Jr.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106–7110.

within the $\sim$8-ns laser pulse (see Figure 1). A UV absorption increasing in intensity from 300 to 260 nm is also formed within the excitation pulse; however, this band demonstrates no decay or chemical reactivity. This absorption overlaps with the UV absorption band of phenanthrene and is attributed to the "instantaneous" generation of **2**. It must be noted that every effort was made to directly detect :CCl$_2$ (especially in the 440–560-nm range) by varying the experimental conditions, e.g., precursor concentration, solvent, saturating gases, laser power, and laser configuration. If :CCl$_2$ has an absorption band in this region,[9] it is "overwhelmed" by the absorptions of triplet phenanthrene.

Recently, Platz and co-workers have demonstrated that ground-state singlet carbenes react with pyridine to form pyridinium ylides,[13] which possess intense absorptions that have successfully been used to competitively measure both the inter- and intramolecular kinetics of several "invisible" alkylchlorocarbenes.[13,14] Similar to the absorption spectra of the pyridinium ylides of methylchlorocarbene (λ_{max} = 360 nm),[14a] *tert*-butylchlorocarbene[13] (λ_{max} = 376 nm), benzylchlorocarbene[14b] (λ_{max} = 379 nm), and cyclopropylchlorocarbene[14c,d] (λ_{max} = 370 nm), LFP of 1×10^{-4} M **1** in the presence of pyridine[15] results in the absorption spectrum of the pyridinium ylide of dichlorocarbene (**4**) having an absorption maximum at 390 nm (see Figure 1).

Again, phenanthrene is "instantaneously" formed,[16] as evidenced by the UV absorption band of **2** (vide supra); however, it is possible to minimize interference from reexcitation of **2** and monitor the absorption of pyridinium ylide **4** in air-saturated C_6H_{12} since there should be no observable reactivity of either singlet :CCl$_2$ or the zwitterionic ylide **4** with molecular oxygen.[17] Therefore, the bimolecular rate constant for the reaction of :CCl$_2$ with pyridine, k_p, $(7.90 \pm 0.23) \times 10^9$ M^{-1} s^{-1}, is readily obtained (eq 1) by monitoring the pseudo-first-order growth rate of **4**, k_{exptl}, at various pyridine concentrations,

$$k_{exptl} = k_o + k_p[\text{pyridine}] \qquad (1)$$

where k_o represents the rate of decay of :CCl$_2$ in the absence of pyridine.[18] The absolute bimolecular quenching rate constants of :CCl$_2$ with several olefinic substrates (see Table I) are also readily obtained by using the competitive "probe" technique,[19] by monitoring changes in k_{exptl} at an experimentally optimum concentration of pyridine,[20] 1.23×10^{-4} M, with added quencher: $k_{exptl} = k_o + k_p[\text{pyridine}] + k_q[\text{olefin}]$.

The absolute kinetic data presented in Table I demonstrate the electrophilic nature of :CCl$_2$ by the marked decrease in reactivity of :CCl$_2$ toward olefins of decreasing substitution. The relative rates of :CCl$_2$ with $Me_2C{=}CMe_2$, $MeCH{=}CMe_2$, *trans*-$MeCH{=}CHEt$, c-C_6H_{10}, and $CH_2{=}CH$-*n*-C_4H_9 have been reported to be 53.7, 23.5, 2.14, 1.00, and 0.19, respectively.[21] It must be noted, however, that the two studies are *not* directly comparable since, in the relative studies, :CCl$_2$ is generated by alkoxide-induced α-elimination (−10 to −20 °C), where carbenoid involvement is possible.[22] Nevertheless, the supporting trends verify the placement of :CCl$_2$ as an electrophile on the "carbene selectivity spectrum" of Moss.[1] However, it is interesting to point out a discrepancy in the empirical correlation. Namely, the absolute rate constants of :CCl$_2$ are greater than those measured[23] for PhC̈Cl (see Table I). Recent experiments[24] have demonstrated, however, a more "amphiphilic" character of PhC̈Cl with substantial reactivity toward electron-deficient olefins.[25]

In summary, a long-awaited clean photolytic source of :CCl$_2$ has been presented. Although :CCl$_2$ still eludes direct observation, the well-documented pyridinium ylide probe technique has been used to successfully measure the first absolute kinetics of this most important carbene.

Currently, other chemical, kinetic, and energetic aspects of :CCl$_2$ reactivity are being pursued.

Acknowledgment. This is Notre Dame Radiation Laboratory Document No. NDRL-3250. We thank the Office of Basic Energy Sciences of the Department of Energy for support and the National Science Foundation for support of the work done at the University of New Hampshire.

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(15) Pyridine (Fisher Scientific) was freshly distilled prior to use.

(16) Continuous-flow cells were used in all LFP experiments.

(17) Ylide **4** has a lifetime of $\sim$35 μs and, indeed, demonstrates no reactivity toward O$_2$; however, it is quenched by the dipolarophile diethyl fumarate with a rate constant of $(7.42 \pm 0.20) \times 10^7$ M^{-1} s^{-1}.

(18) k_o can only be estimated to be $\leq 1 \times 10^5$ s^{-1} from the intercept, $(3 \pm 8) \times 10^4$ s^{-1}, of the pyridine quenching plot.

(19) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(20) Under typical experimental conditions (3-mm sample-cell path length), the OD of pyridine at 266 nm was 0.16, as compared to ≥0.8 for the OD of precursor **1**. Furthermore, no transient species were detected upon 266-nm LFP of 1.23×10^{-4} M pyridine in C_6H_{12}.

(21) Doering, W. v. E.; Henderson, W. A., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 5274–5277.

(22) For aspects of carbenoid formation, see, for example: ref 2a, pp 79–83; ref 2b, pp 82–84; and ref 2d, pp 285–288.

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(25) Also, as a referee most correctly pointed out, the high reactivity observed for :CCl$_2$ is most likely a consequence of a very low LUMO for :CCl$_2$, as predicted by FMO theory.[26]

(26) See: Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15.

Viability of the [Ni^{III}(SR)$_4$]$^-$ Unit in Classical Coordination Compounds and in the Nickel–Sulfur Center of Hydrogenases

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Received January 23, 1989
Revised Manuscript Received January 18, 1990

Recent vigorous research activity directed at elucidating the structural, reactivity, and physical properties of nickel–thiolate coordination compounds has been prompted by the discovery of a nickel–sulfur center in numerous hydrogenase enzymes.[1] Cumulative chemical and spectroscopic evidence suggests that the nickel in these hydrogenases is capable of catalyzing both the reductive formation and oxidative cleavage of dihydrogen: $H_2 \rightleftarrows 2H^+ + 2e^-$. Nickel EXAFS studies of these hydrogenases suggest that the nickel is coordinated to approximately four sulfurs in either a distorted octahedral or square-pyramidal array.[2] In their isolated states, the nickel-containing hydrogenases exhibit characteristic rhombic ESR spectra which have been assigned to a Ni(III) center.[1] Remarkably, the redox potentials for the Ni(III)/Ni(II) couple of these hydrogenases occur in the range of ca. −0.150 to −0.400 V vs NHE (−0.390 to −0.640 V vs SCE),[1] which is in striking contrast to the more positive values (+0.50 to +1.50 V vs SCE) reported for the Ni(III)/Ni(II) couple of

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