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Reaction of Phenylchlorocarbene and Diphenylcarbene with the Carbon–Chlorine Bond: Kinetics and Mechanisms[1]

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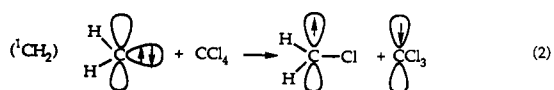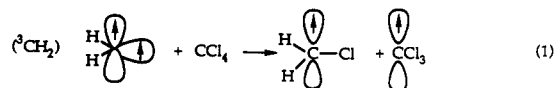Columbus, Ohio 43210. Received September 3, 1991*

Abstract: The reactions of phenylchlorocarbene (PCC) and diphenylcarbene (DPC) with carbon–chlorine bonds were investigated by laser flash photolysis techniques, product studies, and electrochemical methods. The data with both carbenes are consistent with a polar chlorine atom transfer to form radical pairs. The PCC reaction can be thought of as an inner sphere electron transfer from the carbene to the carbon–halogen bond in which there is partial carbon–halogen bond formation in the transition state. The transition state is thought to involve a crossing between closed- and open-shell singlet surfaces. The data obtained in the reaction of DPC with chlorine donors resembles the data obtained with PCC but is more difficult to interpret because the multiplicity of the state reacting with the C–Cl bond is unclear.

I. Introduction

The chlorine atom transfer reactions of free radicals are very well studied processes.[5] Thus it is not surprising that the carbenic variant of this process is known as well. The reaction of methylene with carbon tetrachloride was studied in detail by Urry and Eiszner in 1951.[6] A tetrachloride product is formed in a radical chain decomposition involving the transfer of a chlorine atom to methylene.

$$4 \; \overset{H}{\underset{H}{\diagup}}{=}N_2 \; + \; CCl_4 \; \xrightarrow{\;\Delta\;} \; C(CH_2Cl)_4$$
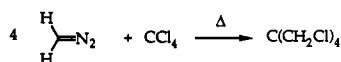
Roth has used the CIDNP technique in an elegant manner to study the reactions of many types of carbenes with chlorocarbons.[7] It is clear that both the singlet and triplet states of methylene can abstract chlorine atoms from suitable donors.

$$(^3CH_2) \quad \overset{H}{\underset{H}{\diagup}} + CCl_4 \longrightarrow \overset{H}{\underset{H}{\diagup}}C{-}Cl \; + \; CCl_3 \qquad (1)$$

$$(^1CH_2) \quad \overset{H}{\underset{H}{\diagup}} + CCl_4 \longrightarrow \overset{H}{\underset{H}{\diagup}}C{-}Cl \; + \; CCl_3 \qquad (2)$$

The reaction of $^3CH_2$ with CCl_4 is easily recognized as a simple variation of the free radical chlorine atom transfer reaction. However, the simple process depicted in eq 2 masks a deeper complexity. It is not immediately obvious how the electrons of the closed-shell singlet state reorganize along the reaction coordinate to form the open-shell singlet radical pair product. This has prompted this study of the reaction of phenylchlorocarbene (PCC), which has a singlet ground state, and diphenylcarbene (DPC), which has a triplet ground state, with carbon–chlorine bonds.

The data with PCC is consistent with inner sphere electron transfer[8] from the carbene to the halocarbon, with partial bond
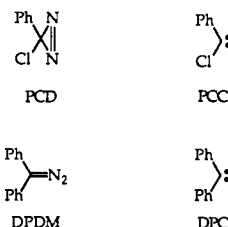
formation between the carbene carbon and the migrating chlorine atom in the transition state. The transition state is thought to involve a crossing between open- and closed-shell surfaces. The data obtained with DPC resembles the results obtained with PCC but is more difficult to interpret because the multiplicity of DPC involved in the chlorine atom transfer reaction is not known with certainty.

II. Phenylchlorocarbene (PCC)

Product Analyses. Photolysis of phenylchlorodiazirine (PCD) in carbon tetrachloride produces three products, consistent with chlorine atom transfer and radical pair formation (Scheme I), in addition to some azine. Similar results were obtained in CCl_3CN (Scheme II). The products were identified by GC–MS–FTIR techniques.

Laser Flash Photolysis. Unfortunately there is severe overlap between the UV absorption maxima of PCC[9] and α,α-dichlorobenzyl radical 1.[10] This prevents clean monitoring of either the disappearance of PCC or the formation of radical 1 and necessitates the use of the pyridine ylide probe method (Scheme III).[11] Pyridine ylide 8 has several desirable properties for a probe of the dynamics of PCC, a lifetime of many microseconds, intense molar absorptivity, and an absorption maximum far removed from that of either PCC or 1.

The absolute rate of formation of 8 following LFP is exponential and can be fit to yield an observed rate constant, k_{obsd}, which can be related to the mechanism of Scheme III as given in eq 3,[11]

$$k_{obsd} = k_{PYR}[PYR] + k_0 \qquad (3)$$

where k_0 is the sum of all first-order and pseudo-first-order processes which consume PCC in the *absence* of pyridine. We

(1) It is with the greatest pleasure that we dedicate this paper to Professor Shelton Bank on the occasion of his 60th birthday for first teaching us about the movement of electrons, singly and in pairs.

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(4) A portion of this work has been communicated previously, see: Jones, M. B.; Jackson, J. E.; Soundararjan, N.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 5597.

(5) Batt, L. *Chemical Kinetics of Small Organic Radicals*; Vol. IV Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. IV, p 1.

(6) (a) Urry, W. H.; Eiszner, J. R. *J. Am. Chem. Soc.* **1951**, *73*, 2977. (b) Urry, W. H.; Eiszner, J. R.; Wilt, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 918. (c) For a review, see: Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 11, Section VI, p 442.

(7) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

(8) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1988; CH II, p 12.
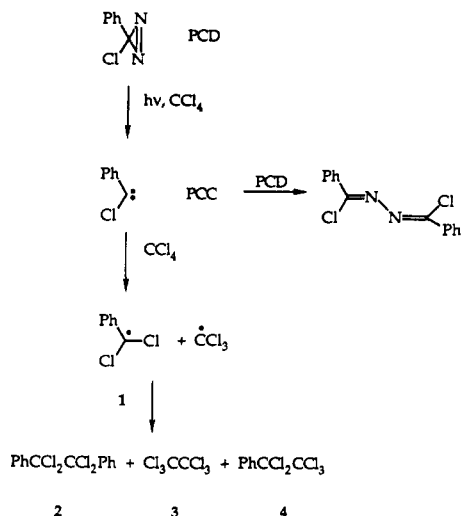
(9) Moss, R. A.; Turro, N. J. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 213.

(10) Brocklehurst, B.; Porter, G.; Savadatti, M. I. *Trans. Faraday Soc.* **1964**, *60*, 2017.

(11) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

(12) The pyridine ylide probe method and the kinetic formalism was developed by Scaiano; see: (a) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828. (b) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431. (c) *Ibid.* **1978**, *59*, 246.

Scheme I

Figure 1. Effect of dielectric constant (ϵ) of the solvent upon the rate constant of reaction of phenylchlorocarbene with trichloroacetonitrile at ambient temperature.

Figure 2. Effect of the reduction potentials of CCl_4, Cl_2CHCN, Cl_3CCN, and $Cl_2C(CN)_2$ upon the rate constants for reaction with PCC in acetonitrile at ambient temperature.

Table I. Absolute Rate Constants for Reaction of Phenylchlorocarbene with Alkyl Halides at 293 K

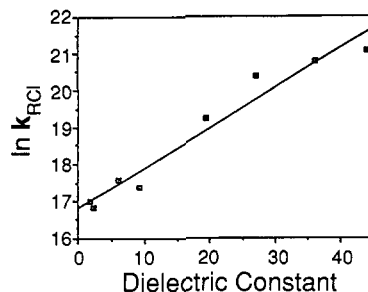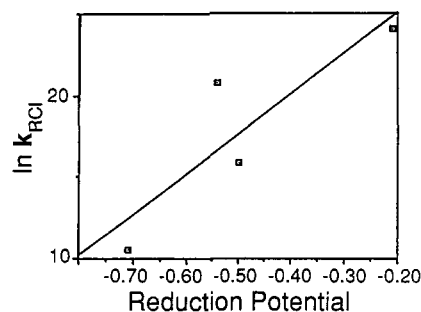| substrate	solvent	$E_{RED}{}^c$ (V)	k_{RCl} (M^{-1} s^{-1})
CCl_4	CH_3CN	−0.71	$(3.83 \pm 1.51) \times 10^4$
Cl_2CHCN	CH_3CN	−0.50	$(7.76 \pm 0.50) \times 10^6$
Cl_3CCN	$C_6H_5CH_3$		$(2.06 \pm 0.14) \times 10^7$
Cl_3CCN	CH_3CN	−0.54	$(1.06 \pm 0.06) \times 10^9$
$Cl_2C(CN)_2$	$C_6H_5CH_3$		$(8.45 \pm 1.42) \times 10^9$
$Cl_2C(CN)_2$	CH_3CN	−0.21	$(2.60 \pm 0.33) \times 10^{10}$
CF_3CCl_3	CH_3CN		a
Cl_3CCO_2Et	CH_3CN		a
Cl_3CBr	$C_6H_5CH_3$		$(7.54 \pm 0.01) \times 10^9$
Cl_3CBr	CH_3CN	−0.49	$(2.65 \pm 0.01) \times 10^{10}$
NCS^b	$C_6H_5CH_3$		$(1.15 \pm 0.08) \times 10^{10}$
NCS^b	CH_3CN	−0.10	$(1.67 \pm 0.01) \times 10^{10}$
CF_3CH_2I	n-C_6H_{14}	−1.18	$(2.06 \pm 0.37) \times 10^8$
CH_3CH_2I	n-C_6H_{14}	-2.48^d	$(3.66 \pm 0.56) \times 10^6$

^{a} Too slow to measure. ^{b} *N*-Chlorosuccinimide. ^{c} Measured in acetonitrile. ^{d} Estimated, see ref 19.

have previously demonstrated that plots of k_{obsd} versus [PYR] are linear and their slopes yield k_{PYR}, the absolute rate constant for the reaction of PCC with pyridine. Upon LFP of PCD in the presence of both pyridine and a chlorine atom donor, the carbene partitions between ylide formation and chlorine atom abstraction. Under these conditions eq 4 is valid,

$$k_{obsd} = k_0 + k_{PYR}[PYR] + k_{RCl}[RCl] \qquad (4)$$

and plots of k_{obsd} versus [RCl] at constant [PYR] should be linear with slopes equal to k_{RCl}, the absolute rate constant for chlorine atom abstraction.

Absolute rate constants for the reaction of PCC with various halogen donors are given in Table I. It is clear from this table, and not very surprising, that bromides react faster than chlorides. There is clearly a polarity effect in the carbene reaction with carbon–halogen bonds because iodine is transferred from CF_3CH_2I more than 50 times more rapidly than from CH_3CH_2I. In fact, Bordwell[13] has used this pair of reagents for distinguishing S_N2 from electron-transfer processes. CF_3CH_2I is much less reactive than CH_3CH_2I in S_N2 processes but is much more reactive than CH_3CH_2I in electron-transfer processes. An electron-transfer component to the chlorine atom transfer reaction is further implicated by the fact that successive replacement of the chlorines of CCl_4 by the cyano group leads to a dramatic rate acceleration; $k_{RCl}(CCl_2(CN)_2) > (CCl_3CN) > (CCl_4)$. Charge development in the chlorine atom transfer reaction is also indicated by the solvent effect. Chlorine is transferred from CCl_3CN in acetonitrile more than 50 times more rapidly than in hexane. To our knowledge this is the largest solvent effect known on the absolute

(13) Bordwell, F. G.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5470.

Table II. Solvent Effect upon the Absolute Rate Constant of Reaction of Phenylchlorocarbene with Trichloracetonitrile at 293 K

solvent	ϵ	k (M^{-1} s^{-1})
hexane	1.89	$(2.40 \pm 0.28) \times 10^7$
toluene	2.38	$(2.06 \pm 0.14) \times 10^7$
ethyl acetate	6.02	$(4.31 \pm 0.35) \times 10^7$
α,α,α-trifluorotoluene	9.18	$(3.51 \pm 0.28) \times 10^7$
1:1 toluene/CH_3CN	19.3	$(2.25 \pm 0.21) \times 10^8$
propionitrile	27	$(7.03 \pm 0.58) \times 10^8$
acetonitrile	36.2	$(1.06 \pm 0.06) \times 10^9$
sulfolane	44	$(1.39 \pm 0.14) \times 10^9$

Table III. Absolute Rate Constants for Reaction of *p*-Substituted Phenylchlorocarbenes with Trichloroacetonitrile in Toluene at Ambient Temperature

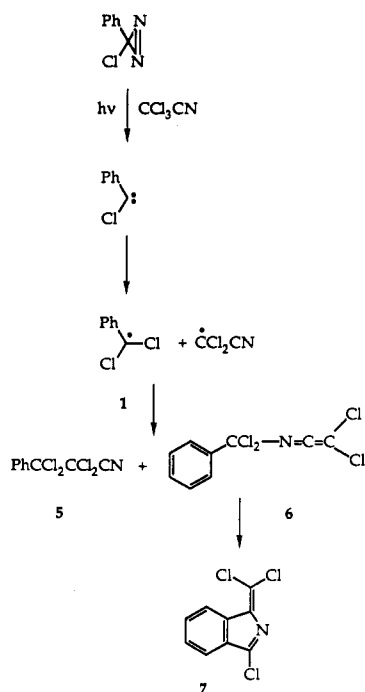| para substituent	k_{RCl} (M^{-1} s^{-1})	k_{rel}	$k_{rel}(TME)^a$	$k_{rel}(PYR)^b$
NO_2	$(2.14 \pm 0.45) \times 10^6$	0.10	$(5.35)^c$	6.04
H	$(2.06 \pm 0.14) \times 10^7$	1.0	1.00	1.00
OCH_3	$(1.14 \pm 0.21) \times 10^8$	5.5	0.05	0.08

^{a} Reference 9, isooctane solvent. ^{b} Reference 15, toluene solvent. ^{c} *p*-CF_3 substituent.

rate of a carbene reaction. In contrast, there is essentially no solvent effect on the rate of reaction of PCC with alkenes[9,14] or pyridine.[15] Positive charge character developing on the migrating chlorine atom is indicated by the very large rate constant of reaction of PCC with *N*-chlorosuccinimide. This reaction basically proceeds at a diffusion-controlled rate. The trends identified in Table I were amplified by more systematic studies reported in other tables (vide infra).
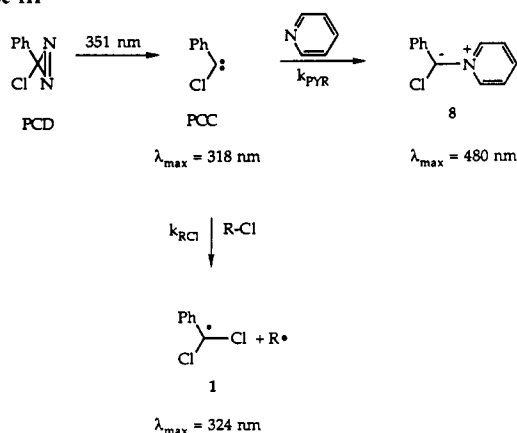
The effect of the variation of solvent polarity on the absolute rate constant of reaction of PCC with Cl_3CCN is presented in Table II. As shown in Figure 1, ln k_{RCl} varies smoothly with the dielectric constant (ϵ) of the solvent. The value of k_{RCl} in sulfolane, the most viscous solvent utilized in this work, is probably diffusion limited due to the relatively high viscosity of this solvent.

(14) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143.
(15) Jones, M. B.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 1694.

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Scheme II

Scheme III

$\lambda_{max} = 318$ nm

$\lambda_{max} = 480$ nm

$\lambda_{max} = 324$ nm

A plot of the ln k_{RCl} versus the reduction potential of the chlorine atom donor is given in Figure 2. Although the relationship is not linear, it is clear that k_{RCl} increases with the ease of reduction of the chlorine donor.

The absolute rate constants of reaction of p-nitro and p-methoxy PCC with CCl_3CN were also measured (Table III).[4] A large substituent effect was observed, which indicated that positive charge develops on the carbene carbon in the transition state of the chlorine atom transfer reaction. It is interesting to note that the direction of the substituent effect on the chlorine atom transfer process is *opposite* to the substituent effect observed in the reaction of PCC with tetramethylethylene[9] or pyridine.[15] In these reactions, the π electrons of TME or pyridine associate with the empty p–π orbital of the carbene.
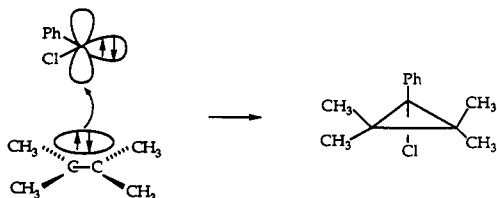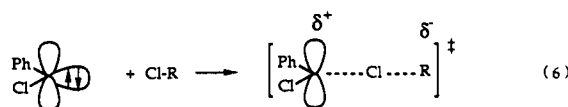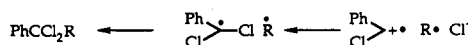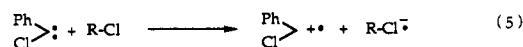
Thus it is clear that it is the occupied, in-plane, σ orbital of PCC which reacts with alkyl chlorides. This immediately excludes halonium ylide formation along the reaction coordinate, leading

to chlorine atom transfer with PCC. Of course this mechanism remains a viable option for other carbenes.[6c]
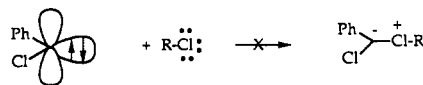
The results are permissive of two mechanistic extremes, electron transfer (eq 5) or polar atom transfer (eq 6).

$$\begin{array}{c}Ph\\Cl\end{array}\!\!\!>: \; + \; R\text{-}Cl \longrightarrow \begin{array}{c}Ph\\Cl\end{array}\!\!\!>\!\!+\bullet \; + \; R\text{-}Cl^{-}\bullet \qquad (5)$$

$$PhCCl_2R \longleftarrow \begin{array}{c}Ph\\Cl\end{array}\!\!\!>\!\!\bullet\text{-}Cl \; \overset{\bullet}{R} \longleftarrow \begin{array}{c}Ph\\Cl\end{array}\!\!\!>\!\!+\bullet \; R\bullet \; Cl^{-}$$

$$\begin{array}{c}Ph\\Cl\end{array} \; + \; Cl\text{-}R \longrightarrow \left[\begin{array}{c}\delta^{+}\\Ph\\Cl\end{array}\!\!\!-\!\!-\!\!-Cl\!\!-\!\!-\!\!-\overset{\delta^{-}}{R}\right]^{\ddagger} \qquad (6)$$
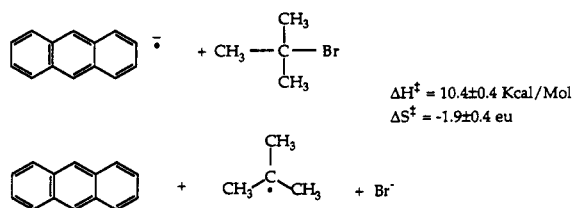
Equations 5 and 6 represent mechanistic extremes differing only in the timing of electron and atom transfer. Mechanisms which are hybrids of eqs 5 and 6 are possible, and the exact composition of this hybrid can vary with both RCl and solvent. This will be demonstrated by considering the activation parameters of chlorine transfer.

Activation Parameters to PCC Reactions with RCl. Savéant[16] has studied the S_N2 reaction of the anthracene radical anion with n-butyl bromide

$+ \; CH_3CH_2CH_2CH_2\text{-}Br$

$\Delta H^{\ddagger} = 7.0\pm0.2$ Kcal/Mol
$\Delta S^{\ddagger} = -19.1\pm1$ eu
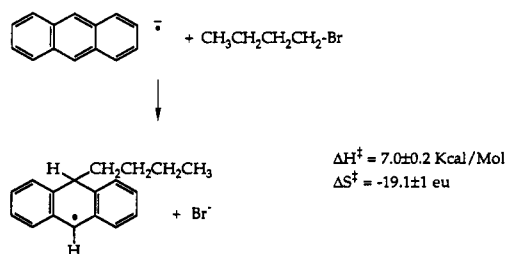
and the electron-transfer reaction of this reagent with *tert*-butyl bromide.

$+ \; CH_3\!-\!\overset{CH_3}{\underset{CH_3}{C}}\!-\!Br$

$\Delta H^{\ddagger} = 10.4\pm0.4$ Kcal/Mol
$\Delta S^{\ddagger} = -1.9\pm0.4$ eu

$+ \; CH_3\overset{CH_3}{\underset{}{C}}CH_3 \; + \; Br^{-}$

The S_N2 process has the lower $\Delta H^{\ddagger}$ value because of partial C–C bond formation. The electron-transfer mechanism has the more positive $\Delta S^{\ddagger}$ value because close association of the reactants and bond formation in the transition state are not required as in the S_N2 transition state. The n-butyl bromide reaction prefers the S_N2 mechanism at low temperature but electron transfer (ET) at high temperature. *tert*-Butyl bromide reacts via the ET mechanism at all temperatures for steric reasons.

The activation parameters for chlorine atom transfer reactions of PCC are given in Table IV. The $\Delta S^{\ddagger}$ values observed with CCl_3CN in toluene and acetonitrile are large and negative and similar to those reported by Savéant.[16] This indicates that there

(16) (a) Andrieux, C. P.; Gelis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509. (b) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M. *J. Am. Chem. Soc.* **1989**, *11*, 1620. (c) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M.; Su, K.-B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (d) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (e) Lexa, D.; Savéant, J.-M.; Su, K.-B.; Wang, D.-L. *J. Am. Chem. Soc.* **1988**, *110*, 7617. (f) Andrieux, C. P.; Gelis, L.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 786. (g) Lexa, D.; Savéant, J.-M.; Schäfer, H. J.; Su, K.-B.; Vering, B.; Wang, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 6162.

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Table IV. Activation Parameters for Reaction of Phenylchlorocarbene with Chlorine Atom Donors Measured over a Temperature Range of -30 to 45 °C

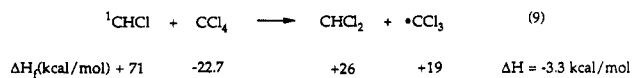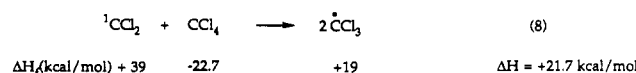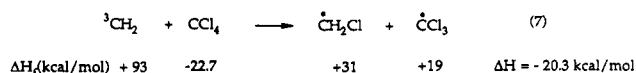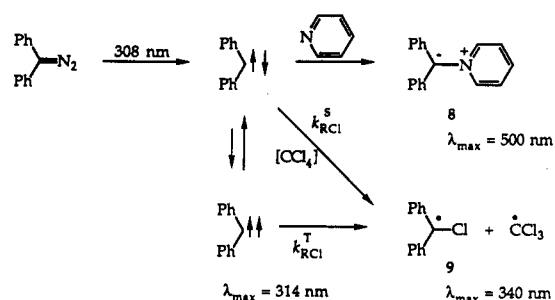| substrate	solvent	$E_a{}^a$	log $(A/M^{-1} s^{-1})$	$\Delta H^{\ddagger\,a}$	$\Delta S^{\ddagger\,b}$
Cl$_3$CCN	toluene	+1.54 ± 0.33	8.40 ± 0.26	+0.94	-22.0
Cl$_3$CCN	CH$_3$CN	-0.46 ± 0.25	8.62 ± 0.20	-1.05	-21.0
Cl$_2$C(CN)$_2$	toluene	+1.45 ± 0.30	11.23 ± 0.24	+0.86	-9.0
Cl$_2$C(CN)$_2$	CH$_3$CN	+1.22 ± 0.63	11.27 ± 0.50	+0.63	-8.8

^{a} Kilocalories/mole. ^{b} Calories/mol·K.

Table V. Activation Parameters for Reaction of Selected Free Radicals with Chlorine and Hydrogen Atom Donors

radical	donor	phase	E_a (kcal/mol)	log $(A/M^{-1} s^{-1})$
c-C$_6$H$_{11}$·[31]	CCl$_4$	gas phase	11.8	8.6
c-C$_6$H$_{11}$·[31,32]	CCl$_4$	solution phase	5.7	
c-C$_5$H$_9$·[33]	CCl$_4$	gas phase	10.3	9.0
n-C$_6$H$_{13}$·[34]	CCl$_4$	hexane	6.1	8.3
2- and 3-C$_6$H$_{15}$·	CCl$_4$	hexane	6.1	
CH$_3$·[35,36]	CCl$_4$	gas phase	9.9 (8.8)	9.1 (10.1)
C$_2$H$_5$·[35]	CCl$_4$	gas phase	9.9	9.4
n-C$_4$H$_9$·[37]	CCl$_4$	n-C$_4$H$_{10}$	5.3	8.6
c-C$_5$H$_9$·[37]	CCl$_4$	c-C$_5$H$_{10}$	4.9	7.3
tert-C$_4$H$_9$·[37]	CCl$_4$	(CH$_3$)$_3$CH	4.7	7.9
CH$_3$·[38]	CH$_3$CH$_3$	gas phase	21.4	11.2
CH$_3$·[39]	n-C$_4$H$_{10}$	gas phase	22.0	9.5
CH$_3$·[40]	C$_6$H$_5$CH$_3$	gas phase	15.8	8.1
Ph$_2$C·[22]	C$_6$H$_5$CH$_3$	toluene	3.6	7.2

is substantial carbene carbon–chlorine atom bonding in the transition state. The reactants are strongly associated as in an S$_N$2 process. The large solvent effect is purely an *enthalpic* effect. There must be more carbene carbon–chlorine bond formation in polar solvents than in nonpolar solvents with CCl$_3$CN. The slightly negative $\Delta H^{\ddagger}$ observed in acetonitrile is not unprecedented. Negative $\Delta H^{\ddagger}$ values have been observed in the reactions of PCC with alkenes[9] and have been attributed to reversibly formed carbene–alkene complexes[9] or to the presence of entropic barriers.[17] In this case it can be easily attributed to a solvent polarity effect as solvents typically become more polar as the temperature is decreased.[18]

Increasing the ease of reduction of the chlorine donor (CCl$_3$CN → CCl$_2$(CN)$_2$) accelerates the reaction rate by making the activation entropy more favorable. It is clear that the CCl$_2$(CN)$_2$ transition state is less associated or "looser" than that of the CCl$_3$CN reaction. The transition state for the CCl$_2$(CN)$_2$ reaction has more ET and less S$_N$2 character than that of the CCl$_3$CN chlorine atom transfer reaction. However, the CCl$_2$(CN)$_2$ reaction can not be a pure ET process: the $\Delta S^{\ddagger}$ is still too negative. This conclusion is corroborated by a study of PCC and 1,4-dinitrobenzene (DNB). 1,4-DNB is as easy to reduce electrochemically as CCl$_3$CN,[19] but it does not react at all with PCC. It is clear that some carbene carbon–chlorine bond formation is necessary in the transition state, even with CCl$_2$(CN)$_2$.

The activation parameters of selected free radical chlorine atom transfer processes are given in Table V. Although the A factors of the free radical chlorine atom transfers are comparable in alkane solvents and in the gas phase, the activation energies are dramatically lower in solution. This has been taken as evidence for charge development; the reaction in solution is a polar atom transfer. The 2 kcal/mol difference in the activation energy of

$$\overset{\cdot}{CH_3} + CCl_4 \longrightarrow \overset{\delta^+}{CH_3}\; \overset{\delta^-}{Cl}\; \overset{\cdot}{CCl_3} \longrightarrow CH_3Cl + \overset{\cdot}{CCl_3}$$
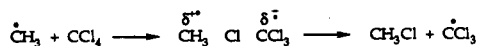
(17) (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555. (b) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4291.

(18) (a) Kosowar, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253. (b) Kamlet, M. J.; Abbound, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. (c) Reichardt, C. *Molecular Interactions*; Ratajcak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 3, pp 241–282.

(19) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Dekker: New York, 1970; Chapters 7 and 11.

Scheme IV

$$^3CH_2 + CCl_4 \longrightarrow \overset{\cdot}{CH_2}Cl + \overset{\cdot}{CCl_3} \quad (7)$$

ΔH_f(kcal/mol) +93   -22.7   +31   +19 ΔH = -20.3 kcal/mol

$$^1CCl_2 + CCl_4 \longrightarrow 2\overset{\cdot}{CCl_3} \quad (8)$$

ΔH_f(kcal/mol) +39   -22.7   +19 ΔH = +21.7 kcal/mol

$$^1CHCl + CCl_4 \longrightarrow CHCl_2 + \cdot CCl_3 \quad (9)$$

ΔH_f(kcal/mol) +71   -22.7   +26   +19 ΔH = -3.3 kcal/mol

$$\overset{\cdot}{CH_2}Cl + CCl_4 \longrightarrow CH_2Cl_2 + \overset{\cdot}{CCl_3} \quad (10)$$

ΔH_f(kcal/mol) +31   -22.7   -21.2   +19 ΔH = -10.5 kcal/mol

Scheme V

λ_{max} = 314 nm λ_{max} = 340 nm λ_{max} = 500 nm
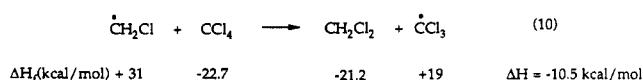
Table VI. Effect of Reduction Potential of Alkyl Chlorides upon the Rate Constant of Reaction with Diphenylcarbene in Acetonitrile at 293 K (Pyridine Ylide Probe Method)

substrate ($E_{RED}{}^a$)	k_{RCl}^{obsd}(DPC)
CF$_3$CCl$_3$	(1.00 ± 0.15) × 10^6
CCl$_4$ (-0.71)	(6.89 ± 0.54) × 10^6
Cl$_2$CHCN (-0.50)	(1.81 ± 0.32) × 10^7
Cl$_3$CCN (-0.54)	(3.56 ± 0.55) × 10^8
Cl$_2$C(CN)$_2$ (-0.21)	(2.14 ± 0.30) × 10^9

^{a} Acetonitrile solvent.

reaction of PCC with CCl$_3$CN in toluene and acetonitrile is consistent with the free radical literature. The similarity in the Arrhenius A values of the reaction of PCC with CCl$_3$CN and of free radical reactions with CCl$_4$ indicates that there are comparable amounts of carbon–chlorine bond formation in the transition states of these two reactions. The much larger A factor of the reaction of PCC with CCl$_2$(CN)$_2$ indicates that there is much less carbon–chlorine bond formation in this system than in the transition states of free radical chlorine atom transfers.

The activation parameters to chlorine transfer are very much smaller with carbenes than those observed in free radical reactions. This is reasonable for triplet methylene (Scheme IV) in which the reaction with carbon tetrachloride is very exothermic. The heat of formation of radical 1 is not known; thus ΔH cannot be calculated for the reaction of PCC with CCl$_4$. However, the reactions of CCl$_2$ and CHCl with CCl$_4$ are calculated to be less exothermic than the reaction of the CH$_2$Cl radical with CCl$_4$, implying that the chlorine atom transfer reactions of PCC should be slower than the corresponding free radical processes.[20] Thus, either the thermodynamics of the PCC reaction are quite different from those of CHCl or else phenylchlorocarbene is more easily

(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.
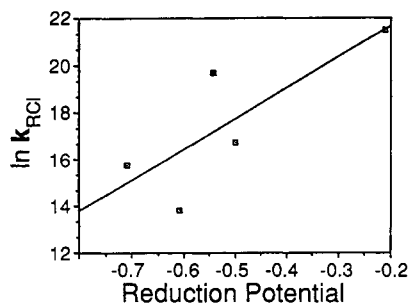
Reaction of Phenylchloro- and Diphenylcarbene

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Figure 3. Effect of reduction potential of the chlorine donor upon the rate constant for reaction with diphenylcarbene in acetonitrile at ambient temperature.

Figure 4. Relationship between rate constants for reaction of diphenylcarbene and phenylchlorocarbene with chlorine atom donors in acetonitrile at ambient temperature: (a) CCl_4, (b) Cl_2CHCN, (c) Cl_3-CCN, (d) $Cl_2C(CN)_2$.

Table VII. Absolute Rate Constants for Reaction of *p,p'*-Disubstituted Diphenylcarbenes with Carbon Tetrachloride in Chlorobenzene at 293 K

R	R'	k (M^{-1} s^{-1})[a]	k (M^{-1} s^{-1})[b]
H	H	$(2.73 \pm 0.35) \times 10^6$	$(3.3 \pm 1.2) \times 10^6$
H	CH_3	$(2.00 \pm 0.45) \times 10^7$	$(1.60 \pm 0.43) \times 10^7$
H	CN	c	$(2.3 \pm 2.4) \times 10^5$
CN	CH_3	$(1.39 \pm 0.80) \times 10^6$	$(4.0 \pm 1.2) \times 10^5$
CH_3	CH_3	$(7.39 \pm 0.75) \times 10^7$	$(7.20 \pm 1.74) \times 10^7$

[a] Monitoring the pyridinium ylide **8**. [b] Monitoring the chlorobenzhydryl radical **9**. [c] This carbene does not react with pyridine to form an ylide at a useable rate.

Table VIII. Solvent Effect upon the Absolute Rate Constants of Reaction of *p*-Substituted Diphenylcarbenes with Carbon Tetrachloride at Ambient Temperature

R	R'	solvent	k (M^{-1} s^{-1})	species monitored
H	H	chlorobenzene	$(2.73 \bullet 0.35) \times 10^6$	8
H	H	acetonitrile	$(6.89 \pm 0.54) \times 10^6$	8
H	CN	cyclohexane	$(3.4 \pm 1.2) \times 10^4$	9
H	CN	acetonitrile	$(1.25 \pm 0.33) \times 10^5$	9

polarized and will more easily tolerate a positive charge in the chlorine atom transfer transition state than will the CH_2Cl radical.

Diphenylcarbene. Diphenylcarbene (DPC), a species with a triplet ground state,[21] is known to abstract chlorine atoms from CCl_4.[22] The reaction rate constant k_{RCl} and its Arrhenius parameters have been reported by measuring the rate of formation of **9** as a function of $[CCl_4]$. This system also suffers from overlapping absorptions of ^3DPC and **9**. This prompted us to remeasure and extend these measurements again using the pyridine ylide probe method (Scheme V).

Absolute rate constants for the reaction of ^3DPC with various chlorine atom donors are given in Table VI. It is clear that k_{RCl} increases with the ease of reduction of the chlorine donor (Figure 3). There is also a reasonable correlation between ln k_{RCl} for PCC, a ground-state singlet carbene, and ln k_{RCl} for ^3DPC (Figure 4).

The effect of substituent on the ^3DPC process mirrors that observed with PCC (Table VII). Electron-donating groups accelerate the reaction rate with CCl_4, and electron-withdrawing groups decelerate the reaction rate. There is a modest solvent effect on the reaction with CCl_4 (Table VIII). The chlorine atom transfer reaction is slightly faster in acetonitrile than in chlorobenzene.

The activation parameters for the reaction of ^3DPC with CCl_4 are reported in Table IX. The electron-donating methyl group accelerates the reaction by lowering the activation enthalpy. The electron-withdrawing cyano group decelerates the reaction with
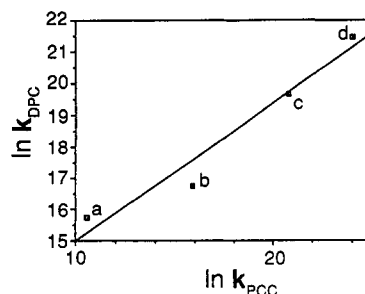
Table IX. Arrhenius Parameters for Reaction of *p*-Substituted Diphenylcarbenes with Carbon Tetrachloride in Chlorobenzene

R	R'	E_a (kcal/mol)	log A	species monitored
H	CN	2.44 ± 0.07	6.08	radical **9**
H	CH_3	0.17 ± 0.17	7.3 ± 0.2	radical **9**
H	H	1.5 ± 0.3	7.4 ± 0.2	radical **9**
H	H	$1.49 \bullet 0.93$	7.80 ± 0.72	ylide **8**

CCl_4 by making both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ less favorable.

III. Discussion

The PCC data requires that there is both positive charge developing on the carbene carbon and partial bond formation between the carbene carbon and the migrating chlorine. The simplest mechanism consistent with these facts is an S_N2 type of displacement on chlorine.
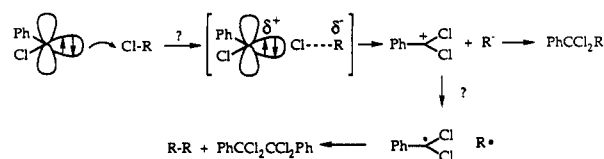
However, this mechanism produces an ion rather than a radical pair, which we expect would immediately collapse to form $PhCCl_2R$. The other products observed, R–R and $PhCCl_2CCl_2$, will not be formed from the alleged ion pair. The only way to salvage this mechanism is to postulate, post facto, that the ion pair immediately undergoes electron transfer to form a radical pair. Kropp has discovered electron-transfer reactions of radical pairs to form ion pairs.[23] However, we are unaware of a precedent for electron transfer in the opposite direction, as required by this mechanism.

A polar atom transfer is consistent with the experimental facts but poses problems in the bookkeeping of electrons. In the transition state there must be a crossing from closed- to open-shell species.
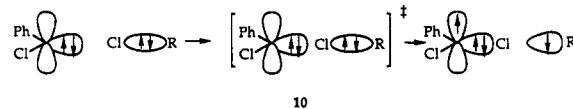
The lowest energy singlet state of methylene is closed-shell (σ^2).[24] The open-shell singlet $(\sigma\pi)$ is calculated to be much higher in energy.[24] Although ab initio calculations of PCC are not available, we expect the same ordering of singlet states in PCC as exists in methylene.

We speculate that the association of the filled σ^2 orbital of PCC with chlorine and its many nonbonding electrons is repulsive. However, association of chlorine with the singly occupied σ orbital

(21) Trozzolo, A. M.; Wasserman, E. *Carbenes*; Moss, R. A.; Jones, M., Jr., Eds., Wiley: New York, 1975; Vol. II, p 185.

(22) (a) Barcus, R. L.; Platz, M. S.; Scaiano, J. C. *J. Phys. Chem.* **1987**, *91*, 695. (b) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283.

(23) Poindexter, G. S.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7142.

(24) For a review, see: Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.
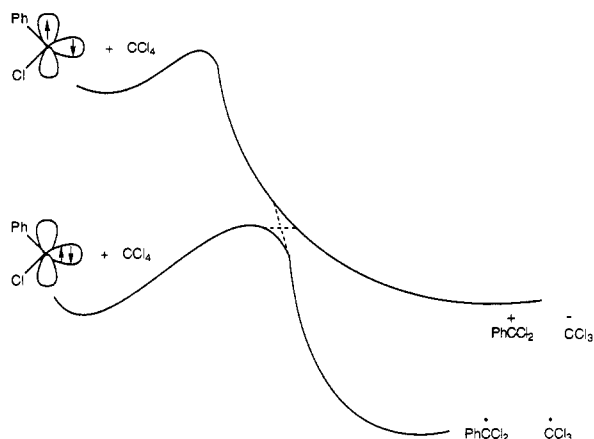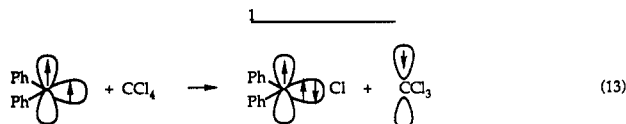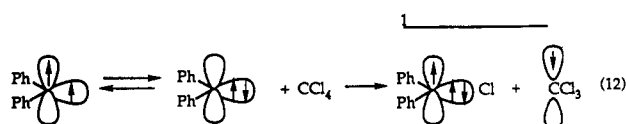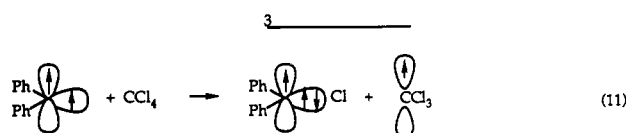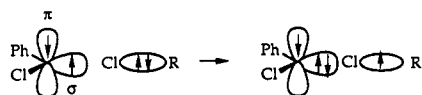
Figure 5. Crossing of closed-shell and open-shell surfaces of singlet PCC along the chlorine atom transfer reaction coordinate.

Scheme VI

$$Ph\text{-carbene} + CCl_4 \longrightarrow Ph\text{-carbene-}Cl + \overset{\cdot}{C}Cl_3 \quad (11)$$

$$Ph\text{-carbene} \rightleftharpoons Ph\text{-carbene} + CCl_4 \longrightarrow Ph\text{-carbene-}Cl + \overset{\cdot}{C}Cl_3 \quad (12)$$

$$Ph\text{-carbene} + CCl_4 \longrightarrow Ph\text{-carbene-}Cl + \overset{\cdot}{C}Cl_3 \quad (13)$$
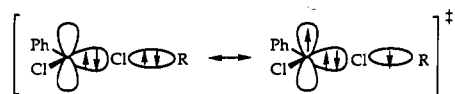
of the open-shell configuration of PCC might be energetically favorable.

This argument predicts that the closed- and open-shell surfaces will cross. The transition state is at the point at which the two singlet surfaces cross (Figure 5).

The crossing point must also have substantial carbene–chlorine bond formation and some charge development to fit the experimental data. The DPC data is even more difficult to interpret because we do not know with certainty whether it is ^{3}DPC or the low-lying singlet state of DPC which is reacting with the chlorine donor.

We can envision three mechanistic possibilities (Scheme VI) for the reaction of ^{3}DPC with chlorine donors. The reaction may be as simple as the reaction of the ground triplet state with CCl_4 (eq 11) by a polar free radical atom transfer to form a triplet radical pair. We have previously[22,25] noted that the Arrhenius parameters of the reaction of ^{3}DPC with CCl_4 are virtually identical to those of the reaction of ^{3}DPC with methanol,[26] a

reaction, regardless of mechanism, which certainly produces a product in a singlet electronic state.[27] This encouraged us to believe that some involvement of ^{1}DPC was indicated in the chlorine atom transfer process.

$$^3DPC + CH_3OH \longrightarrow \underset{Ph}{\overset{Ph}{>}}\underset{OCH_3}{\overset{H}{<}}$$
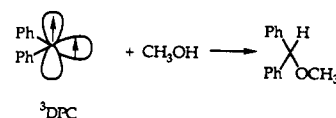
^{3}DPC can produce a singlet radical pair product in its reaction with CCl_4 either by a fast preequilibrium[27] with the low-lying, highly reactive singlet state of DPC (eq 12, Scheme VI) or by a singlet–triplet surface crossing mechanism (eq 13) akin to that of Figure 5. Griller, Nazran, and Scaiano have postulated[26] this type of mechanism in the reaction of ^{3}DPC with methanol.

The simplest interpretation of our data is a mechanism in which the reaction proceeds entirely along the triplet surface (eq 11). In this view, the atom transfer is very similar to a free radical process with some polar character. This is demonstrated by the similarity in the Arrhenius preexponential factors of carbene and free radical chlorine abstraction (viz. Tables V and IX), a small solvent effect, the effect of variation of the chlorine donor, and most dramatically by the effect of substituent on DPC. It is interesting to note that Scaiano and Weir[28] have shown that ^{3}DPC* reacts with carbon tetrachloride with an electron-transfer component.

We can not exclude the possibility that there is some involvement of ^{1}DPC, a state which is intrinsically more reactive than ^{3}DPC, in the chlorine atom transfer reaction, but in the absence of any compelling evidence we feel it wise to prefer the simpler mechanism of eq 11. Such compelling evidence of a change in mechanism might have been provided by very different Arrhenius parameters in the reactions of ^{3}DPC with CCl_4 and with hydrogen atom donors. Although ^{3}DPC reacts faster with CCl_4 than with toluene, the activation parameters[22,26] (Tables V and IX) are not so different as to require a change in mechanism between chlorine and hydrogen atom transfer, and there is no question that the latter reaction does not involve ^{1}DPC.[29]

IV. Conclusion

Singlet phenylchlorocarbene and triplet diphenylcarbene abstract chlorine atoms from suitable donors. Both carbene reactions are accelerated by the presence of electron-donating substituents on the aryl carbene, increasing ease of reduction of the chlorine donor, and an increase in solvent polarity. The data indicates that the transition state has considerable carbene carbon–chlorine bond

(25) Platz, M. S.; Maloney, V. M. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 239.

(26) (a) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198; *Tetrahedron* **1985**, *41*, 1525. (b) Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488. See also ref 24, p 320.

(27) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

(28) (a) Scaiano, J. C.; Weir, D. *Chem. Phys. Lett.* **1987**, *141*, 503. (b) Horn, K. A.; Allison, B. D. *Chem. Phys. Lett.* **1985**, *116*, 114. (c) Scaiano, J. C. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 353.

(29) Closs, G. L. *Chemically Induced Magnetic Polarization*; Lepley, A. R., Closs, G. L., Eds.; Wiley: New York, 1973; p 101.

(30) Gordon, A. J.; Ford, R. A. *The Chemists' Companion*; Wiley: New York, 1972; pp 4–9.

(31) Katz, M. G.; Horowitz, A.; Rajbenbach, L. A. *Int. J. Chem. Kinet.* **1975**, *7*, 183.

(32) Wampler, F. B.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1971**, *3*, 283.

(33) Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1983**, *15*, 905.

(34) Tuan, N. Q.; Gäumann, T. *Radiat. Phys. Chem.* **1978**, *11*, 183.

(35) Matheson, I.; Tedder, J. M.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1982**, *14*, 1033.

(36) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511.

(37) Mawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4721.

(38) Camillerig, P.; Marshall, R. M.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1491.

(39) Pacey, P. D.; Purnell, J. H. *Int. J. Chem. Kinet.* **1972**, *4*, 657.

(40) Dunlop, A. N.; Kominar, R. J.; Price, S. J. W. *Can. J. Chem.* **1970**, *48*, 1269.

formation and charge development. The reaction is an example of inner sphere electron transfer.

V. Experimental Section

Materials. Phenylchlorodiazirine,[9,14] diphenyldiazomethane,[22,26] and their substituted derivatives were prepared by literature methods.

Product Studies of Reactions of Phenylchlorocarbene; Photoactivation. The product mixtures were obtained in one of two ways. A mixture of the carbene precursor was dissolved in either the quencher of interest for liquids or a concentrated solution of the quencher for solid quenchers, taking care that the solvent in the latter case was not reactive toward either the precursor or the carbene (e.g., benzene). This solution could then be placed in a quartz tube equipped with a serum stopper and deoxygenated by bubbling with dry nitrogen. The solution could likewise be placed in a quartz tube, subjected to three freeze–pump–thaw cycles, and sealed under vacuum. The tubes were then photolyzed for ca. 20 min or until the starting material had disappeared. The mixtures were analyzed by gas chromatography. Peaks were identified by coinjection with authentic samples and by mass spectrometry.

Thermolysis of Phenylchlorodiazirine in the Presence of Trichloroacetonitrile. A solution of 1 g (6.6 mmol) of phenylchlorodiazirine and 7 mL (10 g, 69 mmol) of trichloroacetonitrile in 200 mL of dry benzene was refluxed for 2 h under a nitrogen atmosphere. Upon cooling, the mixture was concentrated on the rotary evaporator. A portion of the yellow oil was placed on a column (ca. 18 in.) of silica gel, using hexanes as initial eluent and gradually adding EtOAc to increase the polarity. Collection of small fractions (ca. 5 mL) produced 3-phenyl-2,2,3,3-tetrachloropropionitrile (**5**) as a colorless liquid: IR (neat) 3073, 2246, 1448, 1179, 1058, 945, 793, 711, 623 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) 7.45–7.53 (m, 3 H) 7.96–8.10 (m, 2 H); ^{13}C NMR (500 MHz, acetone-d_6, ppm) 78.37, 114.35, 129.07, 131.08, 132.48, 134.19; exact mass (m/e) calcd for C$_9$H$_5$Cl$_4$N (M$^+$) 268.9572, found 268.7343.

Another portion of the product mixture was subjected to preparatory gas chromatography. The first fraction was the previously isolated 3-phenyl-2,2,3,3-tetrachloropropionitrile (**5**), and the second and third fractions were the remaining two adducts **6** and **7** of the carbene with trichloroacetonitrile. The second fraction was a colorless oil: IR (neat) 3076, 1745, 1600, 1453, 1286, 1158, 1033, 882, 823, 763, 687, 581 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) 7.38–7.70 (m, 11 H), 7.95–8.15 (d of d, 2 H); ^{13}C NMR (500 MHz, CDCl$_3$, ppm) 126.10, 127.95, 128.77, 128.89, 129.92, 130.22, 131.23, 131.44, 135.30, 140.41; exact mass (m/e) found 233.4859 (M$^+$). The third fraction was a yellow oil: IR (neat) 3074, 1651, 1579, 1449, 1228, 1118, 957, 830, 765, 683 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, ppm) 7.40–7.80 (m, 3 H), 7.95–8.15 (m, 1 H); ^{13}C NMR (500 MHz, CDCl$_3$, ppm) 71.78, 126.10, 127.95, 128.67, 128.90, 129.78, 129.92, 130.22, 131.04, 131.23, 131.44, 131.80, 135.30, 135.49; exact mass (m/e) found 168.8721 (M$^+$).

Laser Flash Photolysis Studies. The laser flash photolysis apparatus used a Lumonics Model TE-861 M-4 Excimer laser as the excitation source.[14] Samples could be excited at either 308 (Xe/HCl/He fill gases, maximum pulse energy 110 mJ, pulse width 8–10 ns) or 351 nm (Xe/F$_2$/He, maximum pulse energy mJ, pulse width ns). The monitoring lamp was a 1000-W Xe arc lamp that could be pulsed to increase the intensity of the light. The signals were digitized using a Tektronix 7912 AD programmable digitizer. Optical triggers were added in the later studies between the digitizer and the laser and between the digitizer and the photomultiplier tube to decrease electronic noise. The remainder of the system has been described previously.

Typical stock solutions of the photosensitive compound were prepared in which the photolabile compound had an optical density between 0.1 and 1.0 at the photolysis wavelength. Known volumes of the stock solution (usually 1–2 mL) were added to 1 × 1 cm static cells, either quartz for 308-nm photolysis or Pyrex for 351-nm photolysis, and deoxygenated by bubbling with dry nitrogen or argon. Rate constants were determined by using 8–11 samples of the stock solution containing varying amounts of quencher. Variable-temperature studies were accomplished by connecting a Neslab variable-temperature bath to the sample holder, a copper jacket with windows for the laser and monitoring beams. The jacket was insulated by a glass cylinder containing quartz windows to align the windows on the jacket.

Polarography. A stock solution of 0.5 M LiClO$_4$ in CH$_3$CN (dried over 4-Å molecular sieves overnight) was prepared. A 0.05 M solution of the substrate to be reduced was made using the LiClO$_4$ solution as solvent. The mixture was degassed, a dropping Hg electrode and SCE for reference were added, and the mixture was scanned out to −1.0 V.