Arrhenius Parameters for Hydrogen and Chlorine Atom Abstraction Reactions of Triplet Diphenylcarbene and Dibenzocycloheptadienylidene[1]
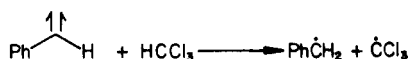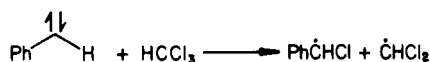
Robert L. Barcus,[2a] Matthew S. Platz,*[2b] and J. C. Scaiano*[2c]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6 (Received: July 1, 1986)

The absolute kinetics of the reaction of triplet diphenylcarbene (DPC) and dibenzocycloheptadienylidene (DBC) were measured with various atom donors as a function of temperature. Diethyl ether and toluene were used as hydrogen atom donors and carbon tetrachloride as a chlorine atom donor. The Arrhenius parameters indicate that triplet DBC reacts directly with carbon tetrachloride but that reaction of DPC with CCl₄ probably involves a triplet–singlet surface crossing.
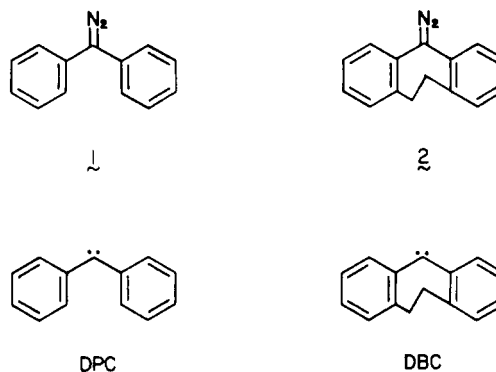
Introduction

It has been long appreciated from product analyses that carbenes will readily abstract chlorine and hydrogen atoms from suitable donors. The free radical nature of the halogen-transfer reactions of methylene with carbon tetrachloride and other polyhalomethanes was established by Urry in the 1950s.[3] Similarly, the photoreactions of methyl diazoacetate with polyhalomethanes were shown to be free radical chain reactions.[4] In the case of diphenylcarbene, Murray and Trozzolo[5] showed that, despite an early report to the contrary,[3b] this carbene reacts with the carbon–halogen bond via halogen abstraction; in this work they also demonstrated the importance of working under conditions (dilute solution) that minimize azine formation. More recently, these reactions have also been studied by the direct spectroscopic methods of CIDNP,[6] EPR,[7] and laser flash photolysis.[8] It is clear from CIDNP and product studies that the hydrogen atom abstraction reaction is unique to triplet carbenes, the preferred reaction mode of singlet carbenes with alkanes being concerted insertion into the CH bond.[9] This is not necessarily true for chlorocarbons; Roth has discovered that both singlet and triplet methylene will abstract a chlorine atom from carbon tetrachloride. In an elegant experiment Roth stuudied the CIDNP produced on photolysis of phenyldiazomethane in chloroform. The data indicated that singlet phenylcarbene reacts by Cl atom abstraction as expected but that triplet phenylcarbene preferentially abstracts hydrogen rather than chlorine from chloroform.[10]

$$Ph\text{-}\overset{\downarrow\uparrow}{C}\text{-}H + HCCl_3 \longrightarrow Ph\dot{C}HCl + \dot{C}HCl_2$$

$$Ph\text{-}\overset{\uparrow\uparrow}{C}\text{-}H + HCCl_3 \longrightarrow Ph\dot{C}H_2 + \dot{C}Cl_3$$

The absolute kinetics of triplet carbene reactions in low temperature matrices have been reported.[7] Photolysis of matrix-
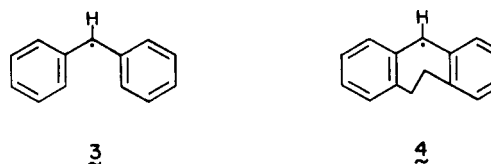
isolated diphenyldiazomethane (**1**) and diazodibenzocyclo-

heptadiene (**2**) generates diphenylcarbene (DPC) and dibenzocycloheptadienylidene (DBC), respectively, both of which can be readily detected by EPR spectroscopy.[11,12] The triplet carbene EPR signals decay slowly in the dark at 77–100 K. Kinetic isotope effects and product studies demonstrated that DPC and DBC react with host matrices by hydrogen atom abstraction. It was postulated further that the mechanism of this hydrogen-atom-transfer process was quantum mechanical tunneling (QMT). The data were fit to an asymmetric Eckart barrier to yield a potential surface. The calculated barrier height (minus suitable zero point corrections) should be equal to the activation energy for a classical atom-transfer process. In this study we report the activation energies of atom-transfer reactions of DPC and DBC in solution phase where QMT corrections are expected to be smaller than in low temperature matrices. The results also serve as a test of the predictive power of the low temperature matrix QMT model.

Results

System Involving Diphenylcarbene and H Atom Donors. Laser flash photolysis (308 nm) of dilute solutions of **1** and **2** in chlorobenzene (typically 10⁻⁴ M) gave the previously reported transient spectra of triplet DPC and DBC.[8] The carbenes were long-lived in chlorobenzene and decayed by a mixture of first- and second-order processes. In hydrogen-atom-donating solvents the carbene lifetimes shorten to 1–2 μs and after this time the transient spectra of the triplet carbenes are replaced by those of the corresponding radicals, **3** and **4**.

(1) Issued as NRCC No. 26371.

(2) (a) Ohio State University. (b) Ohio State University, Camille and Henry Dreyfuss Teacher Scholar. (c) National Research Council.

(3) (a) Urry, W. H.; Eiszner, J. R. *J. Am. Chem. Soc.* **1951,** *73,* 2977. (b) **1952,** *74,* 5822. (c) Urry, W. H.; Eiszner, J. R.; Wilt, J. W. *J. Am. Chem. Soc.* **1957,** *79,* 918.

(4) Urry, W. H.; Wilt, J. W. *J. Am. Chem. Soc.* **1954,** *76,* 2594.

(5) Murray, R. W.; Trozzolo, A. M. *J. Org. Chem.* **1962,** *27,* 3341.

(6) See Closs, G. L. *Chemically Induced Magnetic Polarization,* Lepley, A., Closs, G. L., Eds.; Wiley: New York, 1973.

(7) (a) Lin, C.-T.; Gaspar, P. P. *Tetrahedron Lett.* **1980,** *21,* 3553. (b) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1980,** *102,* 7637. (c) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1981,** *103,* 5503. (d) Wright, B.; Senthilnathan, V. P.; Platz, M. S.; McCurdy, C. W., Jr. *Tetrahedron Lett.* **1982,** *23,* 833. (e) Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *J. Am. Chem. Soc.* **1982,** *104,* 6494.

(8) (a) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984,** *106,* 283. (b) Hadel, L. M.; Platz, M. S.; Wright, B. B.; Scaiano, J. C. *Chem. Phys. Lett.* **1984,** *105,* 539.

(9) Kirmse, W. *Carbene Chemistry;* Academic: New York, 1975.

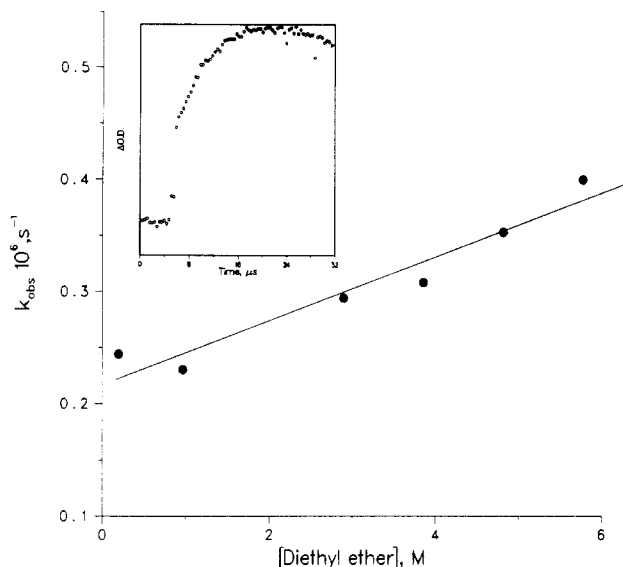(10) Roth, H. D. *Acc. Chem. Res.* **1977,** *10,* 85.

(11) See Trozzolo, A. M., Wasserman, E. In *Carbenes,* Vol. II; Wiley: New York, 1975; p 185.

(12) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1984,** *106,* 4175.

Figure 1. Plot of k_{obsd} vs. [diethyl ether], at room temperature and (insert) growth of benzhydryl radical **3** following laser flash photolysis of **1** in chlorobenzene containing diethyl ether.
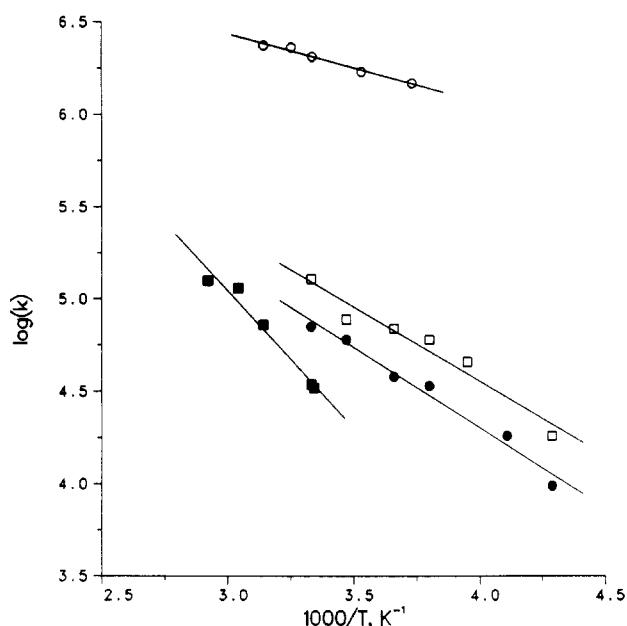

Figure 2. Arrhenius plot illustrating the temperature dependence of the reactions of DPC and CCl_4 (O), DBC and ether (□), DPC and ether (●), and DBC and CCl_4 (■).

The absolute rate of hydrogen atom transfer is most conveniently measured by monitoring the formation of radicals **3** and **4** which absorb at 10–30-nm longer wavelengths than the triplet carbenes. A typical kinetic profile obtained by flash photolysis of **1** in chlorobenzene containing 3.8 M diethyl ether is shown in the insert in Figure 1. The kinetic data were fit to the equation

$$\log \left(\frac{A_\infty - A_t}{A_\infty} \right) = k_{obsd} t \tag{1}$$

where k_{obsd} is the pseudo-first-order rate of radical formation, and A_t and A_∞ are the transient absorptions at time equal to t and at infinity, respectively. The value of A_∞ was measured at the plateau region of Figure 1. It is important to note that the growth lifetime of benzhydryl radical **3** is also equal to the decay lifetime of triplet DPC. The lifetime of triplet DPC is controlled not only by atom abstraction (k), but also by reaction with diazo precursor **1** and by impurities, such as oxygen and water. These contributions to the observed pseudo-first-order rate constant (k_{obsd}) are given by k_0 as

$$k_{obsd} = k_0 + k[\text{atom donor}] \tag{2}$$

TABLE I: Absolute Rate Constants for Reaction of Triplet Carbenes with Hydrogen and Chlorine Atom Donors

carbene	donor	temp, K	k, 10^4 M^{-1} s^{-1}
DPC	ether	300	7.07
		288	6.07
		273	3.80
		263	3.36
		243	1.84
		233	0.98
DPC	toluene	333	10.1
		313	3.58
		300	2.89
		263	1.92
		254	1.30
DPC	CCl_4	318	236
		308	231
		300	202
		283	168
		268	148
DBC	ether	300	13.0
		288	7.74
		273	6.93
		263	6.05
		253	4.58
		233	1.80
DBC	CCl_4	343	12.5
		329	11.6
		318	7.19
		300	3.46
		299	3.30

TABLE II: Arrhenius Parameters for the Reaction of Triplet Carbenes with Various Quenchers in Chlorobenzene–Substrate Mixtures

carbene	quencher	E_a,[a] kcal/mol	log A/M^{-1} s^{-1}[a]	k^{300K}, M^{-1} s^{-1}
DPC	diethyl ether	3.9 ± 0.6	7.8 ± 0.5	7.1 × 10^4
DPC	toluene	3.6 ± 1.7	7.2 ± 1.3	3.8 × 10^4
DPC	CCl_4	1.5 ± 0.3	7.4 ± 0.2	2.0 × 10^6
DPC[b]	methanol	2.5 ± 0.4	9.3 ± 0.3	3.1 × 10^7
DPC[c]	methanol	1.2 ± 0.4	8.2 ± 0.3	2.0 × 10^7
DBC	diethyl ether	3.7 ± 0.9	7.8 ± 0.7	1.3 × 10^5
DBC	CCl_4	6.7 ± 1.5	9.4 ± 1.1	3.5 × 10^4
DBC[d]	methanol	5.0 ± 1.0	9.1 ± 0.8	2.5 × 10^6

[a] All errors reported as ±2σ. [b] In chlorobenzene, from ref 27. [c] In benzene, from ref 27. [d] In toluene, from ref 8b.

Bimolecular rate constants were contained from the slope of a plot of k_{obsd} vs. the concentration of ether. A typical plot is shown in Figure 1; the data are given in Table I. This series of measurements was repeated at different temperatures to give the Arrhenius parameters listed in Table II and Figure 2. The use of flowed solutions of diazo compound was crucial to the success of these experiments.

We have previously reported that DPC reacts more slowly with toluene than with ether.[8] This makes the experimental measurements somewhat more difficult with the former, and as a result the data are of lower accuracy and precision for toluene than for ether.

Reaction of Diphenylcarbene with Carbon Tetrachloride. Laser flash photolysis of **1** in carbon tetrachloride leads to chlorinated radical **5**. Radical **5** is formed in both an instantaneous process

5
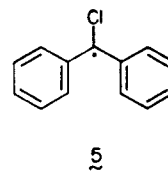
(τ < 10 ns) and in a slow process on the order of a few microseconds. Johnston and Scaiano[13a] and Horn and Allison[13b] have
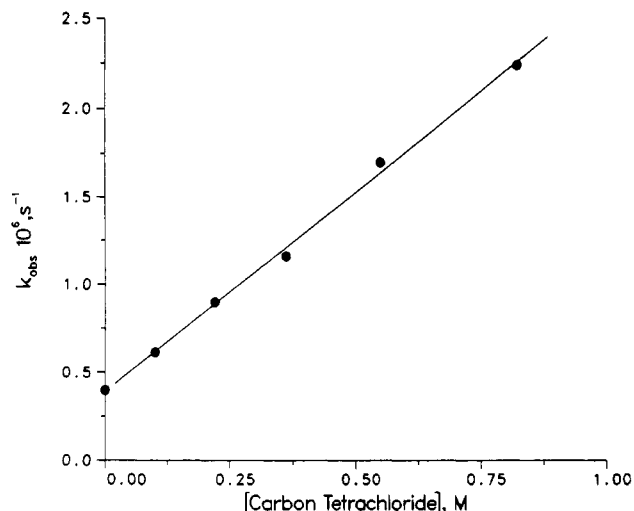
Figure 3. Plot of k_{obsd} for DPC vs. [carbon tetrachloride] at 35 °C.

independently demonstrated that the fast formation of **5** is due to chlorine atom abstraction by the electronically excited triplet state ^{3}DPC*, which is formed by secondary photolysis of ^{3}DPC within the laser excitation pulse.[13] The slow formation of **5** is due to reaction of ground-state ^{3}DPC with carbon tetrachloride. Since the biphasic formation of **5** complicates the analysis of the kinetics of reaction of ^{3}DPC, a probe technique was preferred. We employed flowed solutions of 1×10^{-4} M **1** in 90% chlorobenzene–10% cyclopentane (V/V) containing between 0.1 and 1.0 M carbon tetrachloride. Under these conditions the observed decay of ^{3}DPC (k_{obsd}) is controlled by reaction with cyclopentane (k_H), carbon tetrachloride (k_{Cl}), and the same k_0 term as before.

$$k_{obsd} = k_0 + k_H[c\text{-}C_5H_{10}] + k_{Cl}[CCl_4] \qquad (3)$$

The rate of formation of the benzhydryl radical **3** is also given by k_{obsd} and is dominated by the $k_H[c\text{-}C_5H_{10}]$ term. The value of k_{Cl} could be obtained by measuring k_{obsd} as a function of $[CCl_4]$ at constant concentrations of cyclopentane and diphenyldiazomethane. A plot of k_{obsd} vs. $[CCl_4]$ is given in Figure 3, the slope of which is equal to k_{Cl}. Measurements at several temperatures led to the parameters included in Table II and Figure 2.

Reactions of Dibenzocycloheptadienylidene. Laser flash photolysis of **2** in chlorobenzene–diethyl ether yields DBC; its decay occurs with concurrent formation of radical **4** (Figure 4). The absorption spectra of the carbene and radical overlap extensively; however, at 315 and 350 nm the transient absorptions are dominated by the carbene and the radical, respectively. The kinetics are most easily monitored at 350 nm. The absolute rate of reaction of DBC with ether was measured as for DPC to give the data of Tables I and II. The kinetics of reaction of triplet DBC with toluene were too slow to measure by laser flash photolysis.

The kinetics of reaction of triplet DBC with carbon tetrachloride were also measured as for DPC but in this case 1% 1,4-cyclohexadiene (by volume) was used as a hydrogen donor in order to generate probe radical **4**. The absolute kinetics of DBC with diethyl ether and carbon tetrachloride are given in Table I and the Arrhenius information in Table II and Figure 2.

Discussion

Singlet or Triplet Carbene Reactions? Bethell[14] has postulated that singlet and triplet DPC are in rapid equilibrium in solution at ambient temperatures. Closs[15] and Jones and Gaspar[16] have

SCHEME I
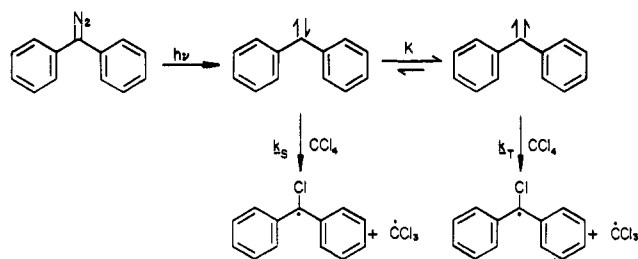
provided a wealth of chemical evidence that spin equilibration in DPC can be more rapid than reaction of either spin state with olefins. The fast equilibrium condition also seems to be appropriate in inert solvents such as benzene containing hydrogen or chlorine atom donors as the absolute rates of reaction of DPC and DBC with these quenchers are comparable to the rates of reaction with typical olefinic trapping agents. Assuming rapid equilibration the observed rate constants (k_{Cl} and k_H) are actually given by

$$k_{H,Cl} = k_T + k_S/K \qquad (4)$$

where k_T, k_S, and K are defined in Scheme I. Laser flash photolysis studies cannot dissect k_H or k_{Cl} into its constituent parts. This can only be accomplished in certain cases by chemical studies or hypothesized on the basis of chemical intuition. Analysis of the products formed in the reaction of DPC with cyclohexane indicates that all of the chemistry can be explained by a single intermediate, ^{3}DPC.[17] We are confident in identifying k_H with k_T for DPC reacting with typical H donors. Based upon work by Moritani, this is probably also true for DBC as well.[18] Thus, the Arrhenius parameters for reaction with ether and toluene can be associated with triplet carbene radical-like hydrogen atom abstraction. The preexponential factors are in the $10^{7.2-7.9}$ M^{-1} s^{-1} range and are much lower than those reported for free radical H-atom abstractions. The preexponential factors for reaction of triplet benzophenone with cyclohexane ($10^{8.66}$ M^{-1} s^{-1}),[19] *tert*-butoxy radical with phenol ($10^{10.66}$ M^{-1} s^{-1}),[20] and tetrahydrofuran[21] ($10^{8.7}$ M^{-1} s^{-1}), of *tert*-butyl radical with tri-*n*-butyltin hydride[22] ($10^{8.43}$ M^{-1} s^{-1}), and of phenyl with tri-*n*-butyltin hydride[23] (10^{10} M^{-1} s^{-1}) are 1 to 3 orders of magnitude larger than those observed for reactions of DPC and DBC. The low preexponential factor may be a consequence of a QMT contribution to the hydrogen-atom-transfer process.[24,25] The activation energies for reaction of ^{3}DPC with ether and toluene are 2–4 kcal/mol lower than predicted by fitting matrix EPR data to an asymmetric Eckart barrier model and assuming quantum mechanical tunneling.[11] The difference may be due to a QMT contribution to the solution phase kinetics.

It is more difficult to associate k_{Cl} with k_T or k_S/K in the case of chlorine atom abstraction than in the case of the H-atom-transfer processes.[5] CIDNP studies on methylene indicate that both singlet and triplet pathways are feasible.[10] Chemical analysis to dissect the product mixture into percentage contributions from specific spin states is of little value because both the singlet and

(13) (a) Johnston, L. J.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *116*, 109. (b) Horn, K. A.; Allison, B. D. *Chem. Phys. Lett.* **1985**, *116*, 114.

(14) (a) Bethell, D.; Stevens, G.; Tickle, P. *Chem. Commun.* **1970**, 792. (b) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23. (c) Bethell, D.; Hayes, J.; Newall, A. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1307.

(15) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(16) Gaspar, P. P.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6108.

(17) Savino, T. G.; Senthilnathan, V. P.; Platz, M. S. *Tetrahedron* **1986**, *42*, 2167.

(18) (a) Moritani, I.; Murahashi, S.-I.; Nishino, N.; Kimura, Y.; Tsubomura, H. *Tetrahedron Lett.* **1966**, 373. (b) Moritani, I.; Murahashi, S.-I.; Ashitaka, H.; Kimura, K.; Tsubomura, H. *J. Am. Chem. Soc.* **1968**, *90*, 5918.

(19) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

(20) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162.

(21) Scaiano, J. C.; Malatesta, V. *J. Org. Chem.* **1982**, *47*, 1455.

(22) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7737.

(23) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4595.

(24) Platz, M. S. et al., to be submitted.

(25) Le Roy, R. J.; Murai, H.; Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2325.

triplet carbene react to give radical pairs which will give rise to similar product mixtures. The Arrhenius parameters themselves do, however, provide considerable insight into the mechanism of chlorine atom transfer; DPC and DBC have nearly identical Arrhenius parameters for the hydrogen atom abstraction reaction with ether but very different parameters for the chlorine abstraction from carbon tetrachloride. The DBC data for chlorine abstraction has a "normal" preexponential factor of $10^{9.5}$ M^{-1} s^{-1} (compared with triethylsilane and CCl_4 with $A = 10^{10.2}$ M^{-1} s^{-1})[26] and an activation energy of 6.7 kcal/mol. DPC, on the other hand, has both a very low A factor equal to $10^{7.4}$ kcal/mol and a very low activation energy of 1.5 kcal/mol.

Methanol is an excellent carbene trap. Very high yields of ethers are obtained on both direct and photosensitized photolysis of **1** and **2** in methanol. The reaction of ^{3}DPC and ^{3}DBC with methanol to give **6** and **7** necessarily requires spin inversion.
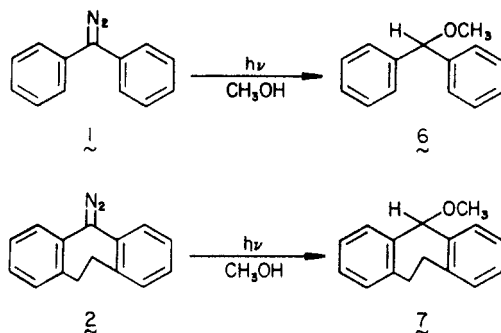
The Arrhenius parameters for the carbon tetrachloride and methanol reactions of DPC and DBC are very similar suggesting similar mechanistic requirements. Nazran, Griller, and Scaiano have proposed that reaction of ^{3}DPC with methanol proceeds by a surface crossing mechanism.[27] We believe that the carbon tetrachloride data for DPC is also most easily interpreted in terms of a mechanism leading into the singlet surface. Such a mechanism would be favored under conditions where the free energy requirements for simple Cl abstraction by the triplet exceed the magnitude of the S–T gap. These conditions are unlikely to be met for DBC with seems to show straightforward triplet behavior, even in the reaction with methanol, which has been the subject of much controversy with DPC and related carbenes.[27]

Judging from the similarity of DPC and DBC toward H abstraction, one would expect the *true* reactivities (k_T of the two triplet carbenes toward Cl abstraction) to be similar too. This is of course not the case: at 300 K DPC reacts with CCl_4 57 times faster than DBC. This in itself suggests a change in mechanism, a postulate that is further supported by the large differences in Arrhenius parameters for the reactions of DPC and DBC with CCl_4 (see Table II). Such a change in mechanism is unlikely to involve a simple thermal population of the singlet carbene manifold: quite simply, the activation energy for DPC is too low for a mechanism of this type and a similar argument applies to the preexponential factor. Instead, we propose a surface-crossing mechanism along the same lines proposed earlier for the DPC–methanol reaction.[27] Under these conditions the singlet and triplet surfaces must cross at a point before the transition state for the triplet carbene chlorine atom abstraction. This is illustrated in Figure 5.

Singlet and triplet methylene have very different geometries; the HCH bond angle in $^1CH_2$ is 102°, while that in $^3CH_2$ is 136°. Increasing the bond angle in $^1CH_2$ leads to a steep increase in energy, while the energy of $^3CH_2$ is less sensitive to angular distortion.[28] It is quite possible that the differences in carbene behavior observed reflect a much larger CCC bond angle in DBC than in DPC, as a result of the ethano bridge. Alternatively, it
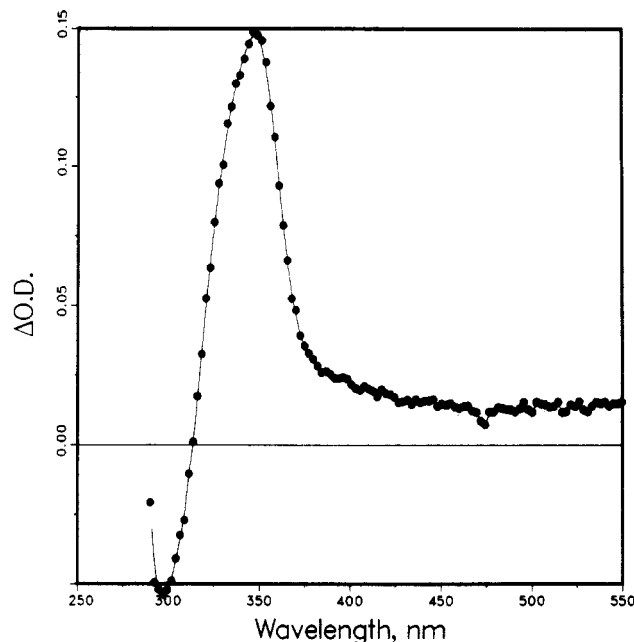
(26) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *106*, 5123.

(27) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(28) See Shavitt, I. *Tetrahedron* **1985**, *41*, 1531, and references therein.

Figure 4. Absorption spectrum of **4** obtained by irradiation of 4×10^{-5} M **2** in 1:1 chlorobenzene–diethyl ether at 293 K. The spectrum was recorded 10 μs after 308-nm laser excitation.
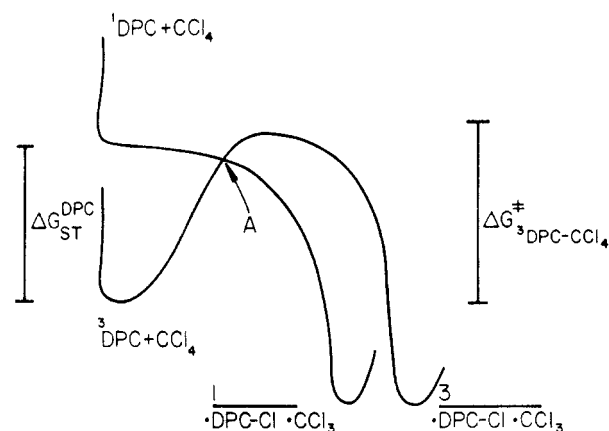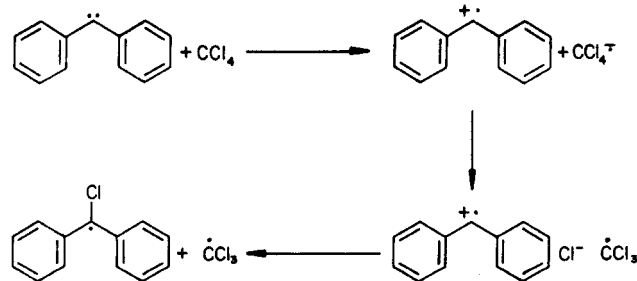
Figure 5. Proposed surface for reaction of DPC with carbon tetrachloride.

is possible that triplet carbene chlorine abstraction has a polar component represented in extreme form by

This does not appear to be a satisfactory explanation for the differences between DPC and DBC in their reactions with CCl_4 because the electron-donating methylene substituents in DBC should stabilize the radical cation representation and lower the activation energy relative to the DPC reaction. This is clearly not the case.

Experimental Section

In a typical experiment a solution of $0.5–1 \times 10^{-4}$ M diazo compound was subjected to laser flash photolysis (308 nm, $\approx$4 ns, up to 80 mJ/pulse, Lumonics Model TE-860-2 operated with Xe–HCl mixtures). The absorption signals were captured by a

Tektronix R-7912 transient digitizer and then transferred to a PDP 11/23 computer which also controls the experiment and provides suitable processing, storage and hardcopy facilities. Further details of the laser flash photolysis system can be found elsewhere.[29] The diazo compounds used in this work were pre-

pared and purified from the corresponding ketones by known procedures.[18,30] The absorption maxima of the carbenes were typically recorded <0.5 µs following the laser pulse.

Registry No. DPC, 3129-17-7; DBC, 15306-40-8.

(29) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(30) Smith, L. I.; Howard, K. L. *Organic Synthesis*; Wiley: New York, 1955; Collect Vol. III, p 351.

Photobromination of C_2H_5Cl In the Presence of C_2H_6. The Heat of Formation of the CH_3CHCl Radical and the $D°(CH_3CHCl-H)$ Bond Dissociation Energy

E. Tschuikow-Roux* and D. R. Salomon

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4
(Received: April 21, 1986; In Final Form: September 16, 1986)

The gas-phase photobromination of C_2H_5Cl in the presence of ethane as competitor has been studied between 32 and 95 °C at total reactant pressures of ~32 Torr and sevenfold hydrocarbon excess over bromine. Under these conditions hydrogen abstraction by bromine atoms from C_2H_5Cl occurs almost exclusively from the CH_2Cl group. Over the temperature range stated, the relative rate constants conform to an Arrhenius rate law, which combined with the known rate parameters for ethane, $\log (A/cm^3\ mol^{-1}\ s^{-1}) = 14.135 \pm 0.056$, $E = 13.66 \pm 0.14$ kcal mol^{-1}, yield for the abstraction of secondary hydrogen in CH_3CH_2Cl $k_1/cm^3\ mol^{-1}\ s^{-1} = 10^{12.182\pm0.091} \exp[-(9.14 \pm 0.16\ \text{kcal mol}^{-1})/RT]$. From an analysis of kinetic and thermochemical data on these and related compounds in the literature the following radical heats of formation and C–H bond dissociation energies are deduced: $\Delta H_f°(CH_3CHCl) = 16.75 \pm 1.0$; $D°(CH_3CHCl-H) = 95.7 \pm 1.0$; $\Delta H_f°(CH_3CHF) = -17.7 \pm 1.1$; and $D°(CH_3CHF-H) = 97.3 \pm 1.1$ kcal mol^{-1}.

Introduction

Recently we reported on the competitive free radical photochlorination of a number of chloro-[1,2] and fluoroethanes[3] where we examined the reactivity trends of Cl-atom attack on hydrogen with the number and position of halogen substitution. This work is presently extended to the photobromination of some of this class of compounds. Whereas, aside from CH_4, the abstraction of H by Cl atoms in hydrocarbons is always exothermic, and usually exothermic for most halohydrocarbons (CH_3CF_3 and CHF_3 are notable exceptions) the corresponding metathesis reactions involving bromine atoms are generally endothermic and have significant activation energies. One therefore expects a higher selectivity for hydrogen abstraction by bromine atoms[4,5] and can anticipate a correlation between the C–H bond strength and activation energy. The selective nature of bromine atom attack in fluorinated ethanes has been demonstrated by Whittle and co-workers:[5,6] in the competitive thermal bromination of C_2H_5F (39–121 °C) and CH_3CHF_2 (25–230 °C) the observed respective bromination products were almost exclusively CH_3CHBrF and CH_3CBrF_2.[5] The strong deactivation toward hydrogen from the β-carbon has been attributed to polar effects with a concomitant reduction in the C–H bond strength at the site of halogen substitution (α-carbon).[7,8]

In the present paper we report on the competitive photobromination of C_2H_5Cl in the presence of C_2H_6. Ethane has been

selected as a reference because (a) the relative rates for hydrogen abstraction by bromine atoms are reasonably compatible, (b) the thermal and photobromination of C_2H_6 has been studied by both competitive[5,9] and direct[10,11] methods, and has been subject of several revisions[6,12] such that the values of the rate parameters, and in particular the activation energy, are sought to be reasonably well established,[11] and (c) the Arrhenius parameters for the reverse reaction ($C_2H_5 + HBr \rightarrow C_2H_6 + Br$) can be deduced from kinetic and thermochemical data in the literature.

Experimental Section

All experiments were carried out in a greaseless static system, using a cylindrical double-jacketed Pyrex reactor connected to a thermostated water circulating bath and protected from room light. Temperatures were varied over the range 32–95 °C and maintained to within 0.1 °C. Pressure measurements were made with a calibrated digital fused quartz Bourdon gauge (Texas Instruments, Model 145). The light source was an ordinary fluorescent lamp placed parallel to the reactor axis. Conversions were kept at less than 3% and irradiation times to 30 min for convenience of sampling. Product analysis was performed with a Varian Vista 6000 gas chromatograph equipped with CDS 401 data system, flame ionization detector (FID), and a 0.5-m-long Porapak N column. Several experiments were carried out to test for dark reactions. When a mixture of C_2H_5Cl, C_2H_6, and Br_2 was left overnight in the shielded reactor at room temperature, no products were found by subsequent GC analysis, while after 2 h at 90 °C trace amounts of bromination products could be detected. In the irradiated $C_2H_5Cl/C_2H_6/Br_2$ mixtures the only carbon-containing products found at temperatures below 90 °C

(1) (a) Tschuikow-Roux, E.; Yano, T.; Niedzielski, J. *J. Phys. Chem.* **1984**, *88*, 1408. (b) Niedzielski, J.; Tschuikow-Roux, E.; Yano, T. *Int. J. Chem. Kinet.* **1984**, *16*, 621.
(2) Tschuikow-Roux, E.; Niedzielski, J.; Faraji, F. *Can. J. Chem.* **1985**, *63*, 1093.
(3) Tschuikow-Roux, E.; Yano, T.; Niedzielski, J. *J. Chem. Phys.* **1985**, *82*, 65.
(4) Benson, S. W. *Thermochemical Kinetics*, 2nd ed; Wiley: New York, 1976.
(5) Coomber, J. W.; Whittle, E. *Trans. Faraday Soc.* **1966**, *62*, 1533.
(6) Amphlett, J. C.; Whittle, E. *Trans. Faraday Soc.* **1968**, *64*, 2130.
(7) Tedder, J. M. *Q. Rev. Chem. Soc.* **1960**, *14*, 336.
(8) Galiba, I.; Tedder, J. M.; Watson, R. A. *J. Chem. Soc.* **1964**, 1321.

(9) Fettis, G. C.; Knox, J. H.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, 4177.
(10) Andersen, H. C.; Van Artsdalen, E. R. *J. Chem. Phys.* **1944**, *12*, 479.
(11) King, K. D.; Golden, D. M.; Benson, S. W. *Trans. Faraday Soc.* **1970**, *66*, 2794.
(12) Coomber, J. W.; Whittle, E. *Trans. Faraday Soc.* **1966**, *62*, 2183.