J. Am. Chem. Soc. 1984, 106, 283-287

dration. Further, in complexes of ammonium ions with polyfunctional ligands such as $CH_3CONHCH(CH_3)COOCH_3$, multiple $-NH^+\cdots O-$, and possibly $-NH^+\cdots N-$, interactions are indicated. The strength of single $-XH^+\cdots Y-$ bonds in complexes involving polyfunctional ligands ranges from 3 to 30 kcal mol^{-1}, and total bonding energies over 40 kcal mol^{-1} in a given complex are observed. The observations suggest that intramolecular and multiple ionic bonds may be significant factors in bioenergetics.

Registry No. c-$C_5H_{10}OH^+$, 88001-03-0; $(CH_3)_2COH^+$, 43022-03-3; $CH_3NH_3^+$, 17000-00-9; $HCONH_2$, 75-12-7; $HCONHCH_3$, 123-39-7; HCONHn-C_3H_7, 6281-94-3; $HCON(CH_3)_2$, 68-12-2; CH_3CONH_2, 60-35-5; $C_6H_5CON(CH_3)_2$, 611-74-5; $CH_3CONHCH_3$, 79-16-3; $CH_3CON(CH_3)_2$, 127-19-5; CH_3CO-Gly-OCH_3, 1117-77-7; CH_3CO-Ala-OCH_3, 3619-02-1; $HCOH^+NH_2$, 50785-80-3; $HCOH^+NH_2\cdot H_2O$, 88001-04-1; $HCOH^+NH_2\cdot 2H_2O$, 88001-05-2; $HCOH^+NH_2\cdot 3H_2O$, 88001-06-3; $HCOH^+NH_2\cdot 4H_2O$, 88001-07-4; $CH_3COH^+N(CH_3)_2$, 52754-55-9; $CH_3COH^+N(CH_3)_2\cdot H_2O$, 88001-08-5; $CH_3COH^+N(CH_3)_2\cdot 2H_2O$, 88001-09-6; $C_6H_5COH^+N(CH_3)_2$, 88001-10-9; CH_3CO-Ala-OCH_3H^+, 88001-11-0; CH_3CO-Ala-$OCH_3H^+\cdot H_2O$, 88001-12-1; CH_3CO-Ala-$OCH_3H^+\cdot 2H_2O$, 88001-13-2; $CH_3COH^+NHCH_3$, 34134-26-4; $(CH_3)_3NH^+$, 16962-53-1; CH_3CO-Gly-OCH_3H^+, 88001-14-3; H_2O, 7732-18-5; CH_3NH_2, 74-89-5; CH_3COOH, 64-19-7; 2-FpyridineH$^+$, 59278-66-9; pyrimidineH$^+$, 17009-95-9; 3-FpyridineH$^+$, 59278-67-0; pyrimidine, 289-95-2.

Study of Hydrogen Atom Abstraction Reactions of Triplet Diphenylcarbene in Solution[1]

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Abstract: Excimer laser flash photolysis of diphenyldiazomethane produces triplet diphenylcarbene (DPC) which can be detected in absorption at 314 nm. In cyclohexane triplet DPC reacts via hydrogen atom abstraction to give the diphenylmethyl radical. The growth of the radical can be cleanly and conveniently monitored at 334 nm. The growth kinetics can be fit to an exponential rate law with a time constant of 1.6 μs. The pseudo-first-order rate constants of formation of the diphenylmethyl radical in various solvents at 300 K are 5.7×10^5 (cyclohexane), 4.8×10^5 (toluene), 2.3×10^6 (tetrahydrofuran), 4×10^6 (cyclohexane), and 2.5×10^6 s^{-1} (triethylamine). The following kinetic isotope effects were measured: 2.6 (cyclohexane–cyclohexane-d_{12}), 6.5 (toluene–toluene-d_8), and 1.5 (cyclohexene–cyclohexene-d_{10}). The observed activation energies for hydrogen atom transfer were 3.2 (toluene), 2.5 (cyclohexane), and 2.9 kcal/mol (cyclopentane).

Introduction

Triplet carbenes have radical-like properties which are a consequence of two singly occupied molecular orbitals. As a result, they can participate in typical free-radical reactions, such as hydrogen or halogen abstractions and radical additions to carbon–carbon double bonds. From the point of view of reaction kinetics, the information available is quite limited. At the outset of this work not a single absolute constant for a triplet carbene atom transfer reaction in solution was known. A limited amount of information on hydrogen abstraction is available for fluorenylidene[4] and 1-naphthylcarbene.[5] In these cases, however, analysis of the kinetics are complicated by rapid singlet $\rightleftharpoons$ triplet equilibration and concurrent singlet insertion reactions.

In this study we report the kinetics of hydrogen atom abstraction reactions of triplet diphenylcarbene. These include reactions with solvents, as well as a variety of olefinic quenchers. We have addressed the question of allylic hydrogen abstraction vs. addition to double bonds. Kinetic isotope effects and temperature dependencies are reported for selected examples.

Previous Studies of Diphenylcarbene

1. Chemical Analysis. Diphenylcarbene (DPC) has been studied extensively. The ground state of DPC is known to be the triplet on the basis of low-temperature ESR work.[6] The solution chemistry of DPC reflects the radical-like properties of the triplet state. Kirmse, Horner, and Hoffmann studied the chemistry of DPC in cyclohexane.[7] These workers found that tetraphenylethane (**5**) was the major reaction product. This product was believed to have been formed via hydrogen atom abstraction of triplet DPC from solvent to give radical pair **3**. The triplet pair can diffuse apart whereupon **5** will be formed upon recombination of diphenylmethyl radicals. In principle, singlet DPC can also react with solvent by direct insertion into a carbon hydrogen bond to give **2a**, but it does not seem likely that singlet DPC can be a precursor of the radical dimer **5**.

Kirmse et al. have also studied the chemistry of DPC in toluene and diisopropyl ether and again observed the formation of radical dimer **5**. This was again interpreted on the basis of hydrogen atom abstraction reaction of triplet DPC. Closs has reexamined the DPC–toluene system in considerable detail.[8] He found a statistical mixture of bibenzyl (**4b**), triphenylethane (**2b**), and tetraphenylethane (**5**). This was compelling evidence that the near-

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[1] Issued as N.R.C.C. publication 22506.

[2] N.R.C.C. visiting scientist.

[3] Alfred P. Sloan Foundation Fellow.

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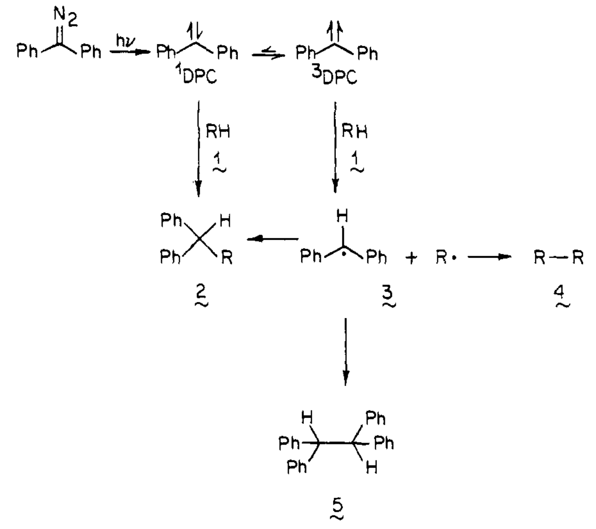
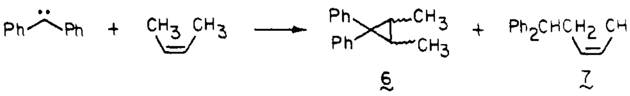


1 (a) R = cyclohexyl
(b) R = benzyl

exclusive chemistry of DPC in toluene is that of the triplet state to give the benzyl–benzylhydryl (**3**) radical pair. The study of this system by Closs led to the development of the radical-pair theory of CIDNP.[8]

The chemistry of DPC with olefins also reflects hydrogen atom transfer processes. Closs and Closs demonstrated that cyclopropanes (**6**) account for no more than 10% of the products formed



from the reaction of DPC with *cis*-2-butene.[9] The major products are olefins (such as **7**) which are derived from abstraction–recombination.

The ratio of cyclopropanes to olefins can be increased with different substrates, such as isobutene.[10] Moss has shown that the ratio of olefins to cyclopropanes is markedly increased in neat polycrystalline matrices at −196 °C with DPC, as well as other carbenes.[11] The product studies of Bethell,[12] Closs and Closs,[13] and Gaspar and Jones[14] have been interpreted in terms of rapid interconversion of DPC spin states in solution at room temperature, although alternative interpretations were not ruled out.[12]

2. Electron Spin Resonance Spectroscopy. Diphenylcarbene has been an attractive candidate for study by direct physical methods, such as ESR. ENDOR work on DPC in a single crystal of 1,1-diphenylethylene resulted in a complete analysis of the isotropic and anisotropic hyperfine interactions. The ENDOR work of Hutchison and Kohler[15] gave a central bond angle of 148°. The dihedral angles between the phenyl planes and the plane defined by the σ bonds of the carbene carbon are 34°. Thus triplet DPC is both bent and nonplanar in the single crystal. However, the structure of DPC observed in the crystal may not be the same as that of DPC in solution because of crystal packing forces. Doetschman and Hutchison studied the kinetics of triplet DPC in a single crystal of 1,1-diphenylethylene and were able to measure the rate constant for cyclopropanation and the associated Arrhenius parameters.[16] This was the first report of an absolute rate constant of a carbene reaction in a condensed phase. In more recent work Platz et al. have studied the absolute kinetics of triplet DPC in glasses and polycrystals at low temperature.[17] The reaction responsible for carbene decay at low temperature was assigned to hydrogen atom abstraction. Interpretation of the matrix data was hampered by site problems resulting in nonexponential decays. The reaction kinetics were said to favor a quantum mechanical tunneling mechanism for atom transfer. The data could be fit to an asymmetric Eckart barrier. The calculated barrier height for the reaction of triplet DPC with toluene was found to be 12.9 kcal/mol. Assuming the loss of all zero-point energy, the model predicts a classical activation energy of ~9 kcal/mol in solution.

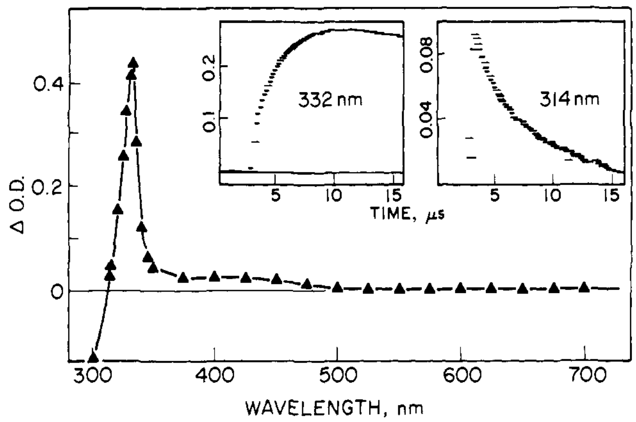
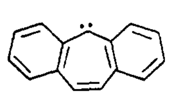


Figure 1. Spectrum of the $Ph_2\dot{C}H$ radical obtained by photolysis of diphenyldiazomethane in cyclohexane at 300 K, recorded between 7 and 10 μs after excitation. Inserts: traces obtained at 332 (left) and 314 nm (right).

3. Electronic Spectroscopy. Closs and Hutchison were able to obtain the electronic absorption spectrum of triplet DPC at low temperature in a single crystal of 1,1-diphenylethylene.[18] The use of an oriented sample allowed these workers to obtain the polarization of the transitions. The spectrum of DPC has also been observed by Moritani. Trozzolo obtained the absorption and emission spectra of triplet DPC in a low-temperature glass.[19] Triplet DPC has a strong absorption band around 300 nm and a much weaker absorption band in the visible.

Flash photolysis has been used extensively in the gas phase to study simple carbenes.[20] The first application of flash photolysis to a diarylcarbene in solution was reported by Moritani in 1968. These workers obtained the absorption spectrum of **8** in paraffin and estimated its lifetime but did not report any rate constants.[21]



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In a pioneering study, Closs and Rabinow obtained the first absolute rate constants for a carbene reaction in solution.[22] These workers measured the rate of dimerization of triplet DPC and the

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rate constants for the reaction of DPC with butadiene and methanol. The butadiene reaction was attributed to triplet DPC, whereas the methanol reaction was assigned to the small, invisible population of singlet DPC present at equilibrium. This led Closs and Rabinow to set the upper limit of the singlet–triplet gap as 2.5 kcal/mol.

In 1980 Eisenthal and Turro[23] measured the rate of singlet to triplet DPC intersystem crossing by laser-induced fluorescence. These workers also reproduced the methanol quenching experiment of Closs and Rabinow[22] and redetermined the equilibrium constant for singlet–triplet equilibration. Upon choosing a somewhat larger value of a diffusion-controlled process, they reported for $\Delta G_{ST} \sim 5$ kcal/mol.[24] Recently Griller, Nazran, and Scaiano[25] have found that the activation energy for the reaction of triplet DPC with methanol in various solvents is much smaller than 4 kcal/mol. This result is inconsistent with the postulated singlet–triplet gap and suggests that the mechanism of this reaction is more complex than was originally suspected.[25]

Results

All experiments were carried out in deaerated solutions using the pulses from an excimer laser operated at 308 nm for excitation. A flow system was used in all experiments involving nondeuterated solvents; for these, various control experiments, described in the Experimental Section, were carried out to ensure the validity of the kinetic parameters obtained.

Reaction with Solvents. When a dilute sample of diphenyldiazomethane, typically $\sim 10^{-4}$ M, in cyclohexane is excited with the 308-nm pulses, we observe the "formally" instantaneous (<5 ns) formation of diphenylcarbene, DPC, which shows a strong absorption around 314 nm. A weak bleaching is observed concurrently in the 500–600-nm region. We attribute this bleaching to the weak visible band of the diazo precursor which is destroyed upon photolysis. As the 314-nm carbene signal decays, frequently in the microsecond time scale, a new species is formed, showing a remarkably strong absorption band with λ_{max} 334 nm. This signal is attributed to the diphenylmethyl radical (**3**) whose spectrum has been previously characterized.[26] High extinction coefficients (and thus strong signals) are not uncommon for resonance-stabilized radicals such as diphenylmethyl. Figure 1 shows the transient spectra obtained after the decay of the carbene is complete ($\sim$10–15 μs); the inserts show the decay of the carbene at 314 nm and the formation of the diphenylmethyl radical (334 nm). Closs and Rabinow[22] also studied the solution-phase flash photolysis of diphenyldiazomethane in cyclohexane. They observed the benzhydryl radical spectrum but could not resolve the growth kinetics of this species.

Kinetic studies can be carried out based on the decay of the signal at 314 nm or on the buildup at 334 nm. In practice, the latter is more suited for detailed study, as the increased separation between excitation and monitoring wavelengths, as well as the decreased overlap between the radical and carbene absorptions, facilitates the experiment considerably. The apparent decay of the 314-nm band is usually considerably slower than the growth at 334 nm. In fact, the diphenylmethyl radical (**3**) also absorbs strongly at 314 nm; thus analysis at 314 nm reflects a composite of three processes: (1) decay of triplet DPC, (2) growth of radical **3**, and (3) the decay of diphenylmethyl radical. Furthermore, this leads to considerable uncertainty in the final absorbance on our time scale at 314 nm. Triplet DPC does not absorb strongly at 334 nm, the maximum of radical **3**. Thus kinetic analysis at this wavelength is more straightforward monitoring only the radical growth (fast) and decay (slow). Hence, our quantitative work was performed at 334 nm. The buildup of the signal at 334 nm is expected, and confirmed, to follow pseudo-first-order kinetics.

Table I. Pseudo-First-Order Kinetics for the Decay of Diphenylcarbene in Several Solvents at 300 K

solvent	k/s^{-1} [a]	k_H/k_D [b,c]
cyclohexane	5.7×10^5	2.6
toluene	4.8×10^5	6.5
tetrahydrofuran	2.3×10^6	
cyclohexene	4×10^6	1.5
methylcyclohexane	7×10^5	
2-methyltetrahydrofuran	3.8×10^6	
triethylamine	2.5×10^6	
cyclopentane	2.2×10^6	

[a] Measured in a flow system, monitored at 332 nm, typically ± 20%. [b] In static cells; should be regarded as a lower limit; see text. [c] k_D refers to the perdeuterated substrate.

Table II. Arrhenius Parameters for the Decay of Diphenylcarbene in Various Solvents

solvent	T range (K)	E_a, kcal/mol	log (A/s^{-1})
toluene	264–343	3.2 ± 0.7	8.0 ± 0.5
cyclohexane	276–327	2.5 ± 0.4	7.5 ± 0.3
cyclohexene	267–339	3.0 ± 0.3	8.7 ± 0.2
cyclopentane	234–317	2.9 ± 0.3	7.9 ± 0.2

Measurements of this type were carried out in several solvents, and the results are summarized in Table I. In all cases a well-defined maximum was detected at 334 nm; in some systems, e.g., toluene, the presence of underlying signals was evident (benzyl absorbs at 317 nm). In a few cases the Arrhenius parameters were also determined; these are given in Table II.

Laser flash photolysis studies which monitor the growth of radicals derived from carbenes give absolute rate constants for carbenic reaction with the solvents. It is possible that the observed rate of carbene decay in an alkane solvent is a composite of both triplet carbene abstraction and singlet carbene processes (such as insertion or abstraction–recombination) if triplet–singlet equilibration is rapid. Studies with fluorenylidene[4] and 1-naphthylcarbene[5] in alkanes have demonstrated that the singlet decay route is dominant in these systems. Thus the observed rate constants for these two carbenes cannot be associated with elementary triplet reaction rate constants. However, we believe that the growth rates observed at 334 nm for reaction of triplet DPC with hydrogen atom donors may well reflect essentially pure triplet processes. This belief is based primarily on the product studies of Closs[8] and Kirmse,[7] which indicate high yields of radical-derived products. Further evidence comes from the CIDNP studies of Closs,[8] and to a lesser extent from the fact that the lifetime of triplet DPC in cyclohexane is 10-fold longer than that of 1-naphthylcarbene and at least 1000-fold longer than that of fluorenylidene in the same solvent. The actual rate constants of hydrogen abstraction are obviously less sensitive to carbene structure than these differences may seem to suggest since in the latter two examples singlet insertion paths have been shown to predominate.[4f,5]

Reaction with Various Solutes. The monitoring techniques used in these experiments are basically the same as indicated above. The experiments are carried out at several reagent concentrations. The experimental pseudo-first-order rate constant, k_{expl}, obtained is plotted against the substrate concentration, according to eq 1 to give k_s

$$k_{exptl} = k_0 + k_s[\text{substrate}] \qquad (1)$$

where k_0 includes all pseudo-first-order reactions which DPC may undergo in any given solvent, in the absence of substrates. Hydrogen abstraction, addition, and/or solvent impurity quenching are typical examples of processes that could be included in k_0. The rate constant k_s includes *all* possible modes *and* sites of attack, and it should not be assumed that, just because the species monitored is the radical, other modes of attack are excluded. This is a common situation in laser flash studies of this type, where all reaction paths are included, regardless of the path actually monitored.[27] For example, in the case of styrene the expected

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Table III. Bimolecular Rate Constants for the Reaction of Diphenylcarbene with Various Substrates at 300 K

substrate	solvent	k_r/M^{-1} s^{-1}	η
carbon tetrachloride	cyclohexane	$(3.6 \pm 0.4) \times 10^5$	
tetrahydrofuran	cyclohexane	$(2.0 \pm 0.3) \times 10^5$	
tetrahydrofuran	benzene	$(1.4 \pm 0.2) \times 10^5$	(1.0)[a]
cyclohexene	cyclohexane	$(2.8 \pm 0.1) \times 10^5$	1.1
cyclooctene	cyclohexane	$(3.3 \pm 0.3) \times 10^5$	
1-octene	cyclohexane	$(1.0 \pm 0.1) \times 10^6$	
2,3-dimethyl-2-butene	cyclohexane	$(2.1 \pm 0.3) \times 10^5$	
styrene	cyclohexane	$(1.4 \pm 0.3) \times 10^6$	
1,4-cyclohexadiene	cyclohexane	$(1.0 \pm 0.1) \times 10^7$	1.3
1,3-cyclohexadiene	cyclohexane	$(2.6 \pm 0.2) \times 10^6$	
1,5-cyclooctadiene	cyclohexane	$(2.0 \pm 1.2) \times 10^6$	0.32
1,3-cyclooctadiene	cyclohexane	$(2.8 \pm 0.1) \times 10^5$	1.1
1,3-octadiene	cyclohexane	$(1.5 \pm 0.1) \times 10^6$	0.15
chloroform	cyclohexane	$(8.4 \pm 0.9) \times 10^5$	
triethylamine	cyclohexane	$(3.4 \pm 1.4) \times 10^5$	1.0

[a] Taken as a reference; see text.

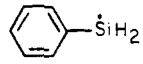
reaction path is addition, not abstraction; the kinetic technique used does not differentiate between these, but simply measures molecular reactivity. In this case the growth of the benzhydryl radical signal is used as a probe, the signal being derived from carbenic reaction with solvent, not styrene. Table III summarizes the data. In systems where cyclohexane was used as solvent, the value of k_0 was typically $\sim 5 \times 10^5$ s^{-1}.

Isotope Effects. Isotope effects were measured using the techniques similar to those in the previous sections. The high cost of several of the deuterated solvents limited the studies to static samples, and to a modest range of temperatures. Rate constants determined in static samples are less accurate than those measured in flow cells. The rate constants measured in static cells are generally about 40% larger than those measured in flow cells. The isotope effects reported in Table I are obtained from matched proton and deuterated static solvent cells. The reported isotope effects may be only the lower limit of the true value. This follows from the fact that in the deuterated solvent the rate of atom transfer is slowed, and other competitive processes such as azine formation or underlying second-order processes may contribute more significantly to the observed rate than in the unmodified solvent.

Discussion

The results obtained in this work (given in Tables I–III) coupled with the product studies of DPC leave no doubt as to the radical-like nature of the processes observed. However, the reactivity observed is at first sight substantially more than expected; the reactivity of Ph_2C: is much larger than that of $Ph_2\dot{C}H$. Our data provide a clear illustration of this effect: while Ph_2C: abstracts from cyclohexane with a lifetime of ca. 1.6 μs at 300 K, the lifetime of the radical produced, $Ph_2\dot{C}H$, is at least 10 times longer, and it is controlled by radical–radical reactions (self-reaction and with c-$C_6H_{11}\cdot$), not by interaction with the solvent. Diphenylmethyl radicals are at the very least 100-fold less reactive than DPC in atom-transfer reactions. The reactivity of DPC exceeds that of alkyl radicals; for example, the rate of reaction of DPC with cyclohexane has been measured as 6.2×10^4 M^{-1} s^{-1} and with THF as 1.5×10^5 M^{-1} s^{-1}. However,[28] the value for reaction of methyl radicals with cyclohexane is $\sim 10^3$ M^{-1} s^{-1}, which is about one order of magnitude faster than comparable reactions of methyl with ethers and only about 30-fold slower than the reaction of phenyl radicals with THF ($k = 4.8 \times 10^6$ M^{-1} s^{-1}).[28] Thus, DPC has a reactivity toward hydrogen abstraction intermediate between those of methyl and phenyl radicals.

It is possible to rationalize the enhanced reactivity of triplet DPC relative to the diphenylmethyl radical on the basis of the following limiting conditions: (a) one of the singly occupied carbene orbitals is pure p, and the other singly occupied orbital is a hybrid containing substantial s character, roughly sp^2; or (b) both singly occupied MO's have the same hybridization (roughly sp^3), each having poor overlap with the aromatic ring. The latter explanation is similar to that encountered in silicon-centered radicals. Radical **9** is pyramidal, the odd electron is essentially localized on silicon, and, consequently, there is almost no difference in the kinetic behavior and spectroscopy of radicals such as $R\dot{S}iH_2$ and $Ph\dot{S}iH_2$.[29]



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Explanation (a) accounts for the enhanced reactivity of triplet DPC by the larger amount of s character present in the in-plane orbital. In this view, triplet DPC is similar to the phenyl radical. This explanation also requires that triplet DPC and diphenylmethyl **3** have identical π systems. Thus one expects similar absorption spectra for these transients. The 20-nm shift in λ_{max} between triplet DPC and **3** suggests at least some differences in their electronic structures. However, there is also a 30-nm shift in absorption maxima between triplet fluorenylidene and the fluorenyl radical,[4] and in these molecules the π systems must be similar because of the enforced planar geometry. The resolution of the MO structure of triplet DPC will probably require ab initio calculations.

In order to estimate the importance of hydrogen abstraction relative to other processes (such as addition), the relative yields of diphenylmethyl radicals were measured. It should be noted that measurements of this type may mask some cage recombination, which could lead to radicals that are not counted by this technique. This is unlikely to introduce a large error in triplet reactions. The radical yields relative to tetrahydrofuran are listed in Table III. The data can only be used as a semiquantiative measure of radical production since other radicals (e.g., cyclohexadienyl) can absorb at 334 nm.[30] Values higher than 1.0 probably reflect these contributions. Values significantly smaller than 1.0 should be taken as evidence for other reaction pathways (e.g., addition to double bonds).

The results in Table II clearly show that attack at the allylic hydrogen plays an important role in the reaction of DPC with olefins, a fact that has been recognized earlier in reports based on product studies.[9] In the case of 1,4-cyclohexadiene, hydrogen abstraction is clearly the dominant process, even if truly quantitative evaluations of the yield are difficult owing to spectral overlap between $Ph_2\dot{C}H$ and c-$C_6\dot{H}_7$ radicals. The excellent hydrogen donor properties of 1,4-cyclohexadiene have also been recognized in their interaction with benzophenone triplets, where abstraction accounts for 94% of the quenching events.[31]

Isotope effects are modest and indicate carbon-hydrogen bond breaking in the transition structure. These observations are rather different from those in the case of fluorenylidene[4] and 1-naphthylcarbene,[5] where low isotope effects, low radical yields, and indications of predominant singlet insertion (from product studies) all combine to support composite rate constants involving singlet as well as triplet reactions. These problems do not seem to be present in the case of DPC, where we suggest that the kinetic and spectroscopic data observed reflect predominantly, or even exclusively, triplet behavior.

The different amounts of singlet and triplet chemistry observed with DPC and fluorenylidene or 1-naphthylcarbene in alkanes are consistent with a larger singlet–triplet gap in the case of DPC. Because of steric respulsions between the ortho hydrogens of DPC, the central bond angle is likely to be large. ENDOR indicates

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that this angle is 148° for triplet DPC.[15] Singlet methylene prefers a small bond angle of 102°, and the singlet energy climbs rapidly upon increasing this angle. Triplet methylene has a bond angle of 138°.[32] The large angles observed for DPC are a consequence of steric repulsion. This selectively raises the singlet energy and increases ΔE_{ST}. The situation is reversed in fluorenylidene, where molecular architecture enforces a small angle, favoring the singlet and lowering the singlet–triplet gap.

The activation energies of Table II are much smaller than those predicted from low-temperature ESR kinetic data which have been fit to an asymmetric Eckart barrier. This could be due to the problem of site inequivalence in the matrix leading to an oversimplified interpretation. Alternatively, one may be looking at reaction trajectories in the matrix that are not ideal, as they may be in solution. This would require the matrix reaction to overcome a larger barrier than the solution process.

The activation energies of Table II are only slightly smaller than the ab initio calculations of Schaeffer for the prototypical reaction,

$$^3CH_2 + CH_4 \rightarrow 2CH_3\cdot \qquad E_a(\text{calcd}) = 7 \text{ kcal/mol}$$

and very much smaller than the barriers calculated by semiempirical methods.[33] The small discrepancy between theory and experiment may be due to an invalid comparison between different carbenes, or to artificially low experimental activation energies (vide infra).

The experimental Arrhenius parameters were determined from the radical growth lifetimes in solution. Side reactions (such as azine formation or reaction with traces of water or oxygen) may become more prevalent at low temperatures. Under these conditions the observable Arrhenius parameters could be lower than those for the abstraction reaction itself.

Experimental Section

Diphenyldiazomethane was prepared according to a literature procedure[34] and purified by sublimation under vacuum. The solvents were purified by standard procedures or used as received when spectrograde solvents were commercially available.

Deaerated samples for the laser photolysis experiments were either contained in or flowed through cells made of 7 × 7 mm^2 square Suprasil tubing. An excimer laser (Lumonics Model TE-860-2) operated with Xe/HCl/He mixtures was used for excitation at 308 nm (~4 ns, up to 80 mJ/pulse). The detection system employed a Tektronix R-7912 transient digitizer to capture the signals that are then transferred to a PDP 11/23 computer which controls the experiment and provides suitable processing, storage, and hardcopy facilities. Further details have been given elsewhere.[35]

Acknowledgment. The authors are indebted to Mr. S. E. Sugamori for technical assistance.

Registry No. Diphenyldiazomethane, 883-40-9; diphenylcarbene, 3129-17-7; cyclohexane, 110-82-7; toluene, 108-88-3; tetrahydrofuran, 109-99-9; cyclohexene, 110-83-8; methylcyclohexane, 108-87-2; 2-methyltetrahydrofuran, 96-47-9; triethylamine, 121-44-8; cyclopentane, 287-92-3; 1-octene, 111-66-0; cyclooctene, 931-88-4; 2,3-dimethyl-2-butene, 563-79-1; styrene, 100-42-5; 1,4-cyclohexadiene, 628-41-1; 1,3-cyclohexadiene, 592-57-4; 1,5-cyclooctadiene, 111-78-4; 1,3-cyclooctadiene, 1700-10-3; 1,3-octadiene, 1002-33-1; chloroform, 67-66-3; deuterium, 7782-39-0; hydrogen, 1333-74-0; chlorine, 7782-50-5; diphenylmethyl, 4471-17-4; carbon tetrachloride, 56-23-5.

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Single-Crystal Polarized Electronic Absorption Spectrum and Ligand-Field Interpretation of the Bonding of Zeise's Salt

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Abstract: The single-crystal polarized spectra of Zeise's salt, $K[Pt(C_2H_4)Cl_3]H_2O$, taken at 10 K are reported. Ligand field and charge-transfer transitions are assigned. The vibronic structure is assigned and excited-state distortions are interpreted. Angular overlap parameters for the ligands are determined. Ethylene is a strong σ donor and a very weak π acceptor toward Pt(II). The relevance of the excited-state assignments to the photochemical reactivity of Zeise's salt is discussed.

Zeise's salt, $K[Pt(C_2H_4)Cl_3]H_2O$, is one of the most intensively studied compounds containing a metal–olefin bond.[1] The Dewar–Chatt model is generally accepted as providing the best description of the metal–olefin interaction.[2,3] The interaction is considered to consist of a σ bond in which the filled π-bonding orbital of the olefin donates electrons to an empty metal d orbital, and a π back-bond in which a filled metal d orbital donates electrons to an empty π-antibonding orbital on the olefin. The relative importance of the σ and π components is still a topic of discussion (vide infra).

Four types of molecular orbital calculations have been performed on Zeise's salt, yielding different interpretations of the metal–olefin bonding. In an extended Hückel calculation,[4] a CNDO type calculation,[5] and an ab initio calculation[6] the σ and π components were calculated to be about equal. A recent Xα-SW SCF calculation[7] suggested that the σ bonding components are

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