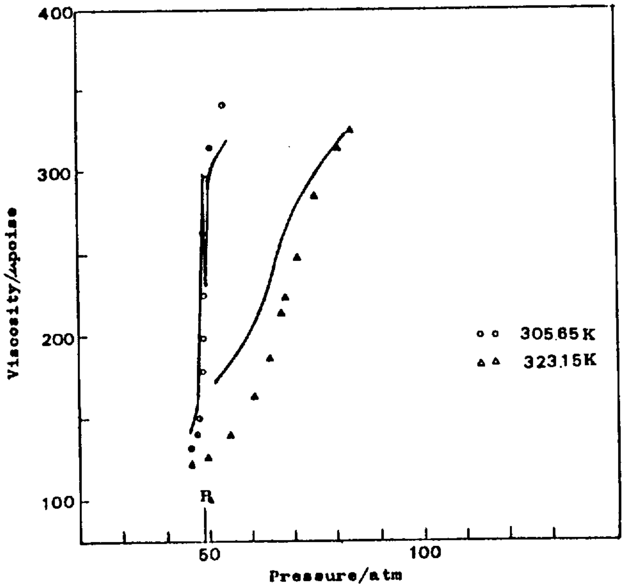

Figure 5. Viscosity of ethane as a function of pressure near the critical point. Calculated; solid line, Observed; circles (T = 305.65 K), triangles (T = 323.15K) (Ref. 11).

experimental methods, such as the capillary flow method for measuring the viscosity, become inaccurate in the critical region due to the large compressibility. Figure 4 shows a plot of the viscosity of carbon dioxide against the pressure at 304.25K 308.15K, and 323.15K. Both the calculated and observed values indicate the rapid increase near the critical point. Figure 5 shows a plot of the viscosity of ethane against the pressure near the critical point. The agreements between theory and experiment are good as those for carbon dioxide.

For the phenomenon of anomalous enhancement in viscosity near the critical point, we can explain as follows. The viscosity of fluids can be considered to be equal to the product of the absolute pressure(kinetic pressure + internal pressure) of fluids and the collision time. Accordingly the magnitude of viscosity depends on the value of the kinetic pressure, internal pressure and the collision time. The viscosity of fluids depends only on the collision time when the fluid has the same kinetic and internal pressure. Near the critical point the phonon velocity is so slow that the viscosity can be seen to present the abnormal behavior because of the large collision time. At the critical point the phonon velocity is zero, so we can see the viscosity of fluids diverge due to the infinitely large collision time. This new methodology of the viscosity interpretation is not the same as the previous theories. We hope this equation is useful to explain the true nature of viscosity of fluids including the critical region.

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The Double Photodissociation of a Geminal, Dichloride

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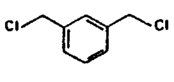
Photolysis of dichlorodiphenylmethane in glassy 2-Me THF at 77K results in the formation of diphenylcarbene and the diphenylchloromethyl radical, which were detected by their fluorescence emission and excitation spectra. The relative yield of the carbene to radical is shown to vary dramatically as a function of irradiation time. The photolability of the radical is also demonstrated. These results were interpreted in terms of a two step mechanism, where the diphenylchloromethyl radical is an intermediate in the formation of diphenylcarbene.

Introduction

The photodissociation of benzylic halides to produce arylmethyl radicals is a well known process. By photolysis of appropriate arylmethyl halides, various arylmethyl radicals including benzyl[1], naphthylmethyl[2] and diphenylmethyl[3] have been produced and spectroscopically characterized. The photodissociation is believed to be initiated by promotion to the $S_2(\pi-\pi^*)$ of the aromatic system. This energy is then transferred into the carbon-halogen bond T (σ^*) state which results in dissociation. Internal conversion of S_2-$S_1(\pi-\pi^*)$ and ISC to the T_1 ($\pi-\pi^*$) state followed by dissociation may also be a contributing pathway.[4] In recent work,[5] we have demonstrated that photolysis of suitable dihalides in rigid organic glasses at low temperature leads to the formation of the corresponding biradicals. It was shown, that photolysis of α,α'-dichloro-*m*-xylene (**1**) or α,α'-dichloro-*o*-xylene (**2**) gives the parent *m*-quinodimethane biradical (**3**) or biradicaloid *o*-quinodimethane (**4**), respectively.



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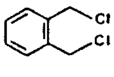

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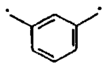

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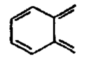

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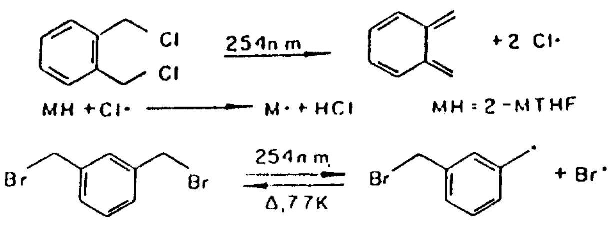
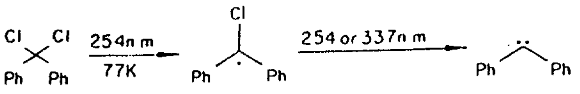
We have proposed a mechanism of double photodissociation wherein the dichloride is photolyzed to yield two Cl atoms and the corresponding biradical. (Scheme 1) We speculated that an initially formed halogen containing monoradical was inititally produced, then further photolyzed under the conditions of the experiment to form a second Cl atom along with the biradical. For the case of the xylylenes however, this was not rigorously demonstrated. Interestingly, photolysis of the corresponding arylmethyl bromides did not result in detectable yields of the radicals or biradicals. Presumably, the Cl atom undergoes further reaction with the matrix preventing the reverse reaction, while the less reactive Br atom simply recombines with the arylmethyl radical.



5 **6**

Scheme 1

We now wish to report that photolysis of the geminal dihalide dichlorodiphenylmethane (**7**), at 77K, leads to the formation of diphenylcarbene (**9**) *via* a similar double photodissociation mechanism. (Scheme 2)



7 **8** **9**

Scheme 2

In this case, evidence supporting the intermediacy of the diphenylchloromethyl radical (**8**) and the sequential nature of the process is presented.

Experimental

Dichlorodiphenylmethane and 2-methyltetrahydrofuran (2-MeTHF) were purchased from Aldrich Chemical Company. 2-MeTHF was refluxed over $KMnO_4$, distilled and dried over molecular sieves prior to use. All fluorescence spectra were obtained on a Perkin-Elmer model LS-5 spectrofluorimeter. The sample compartment of the LS-5 has been modified so that fluorescence spectra can be recorded on samples in a dewar flask at the temperature of boiling liquid N_2. Samples were prepared by syringing 0.5 m*l* of solution into a quartz tube (4mm O.D.). The samples were then degassed by multiple freeze-pump-thaw cycles prior to sealing under vacuum. Irradiation was carried out using either a Rayonet photoreactor (5-RPR-2540 bulbs) or the 337.1nm line of a N_2 laser (Molectron-UV-24 laser operated in repetitive plse mode; 5 pulses/sec; up to 8 mJ per pulse).

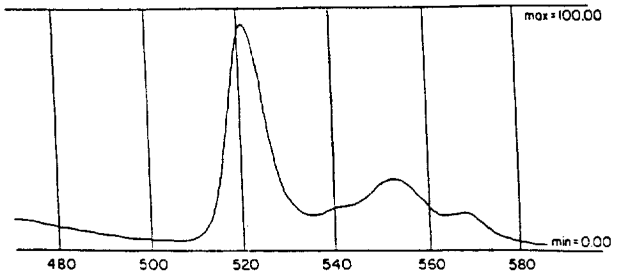


Figure 1a. Fluorescence Emission Spectrum of the diphenylchloromethyl radical (**8**) produced by 254 nm photolysis of 0.01M solution of **7** in glassy 2-MeTHF at 77K. λ excitation was 340 nm.

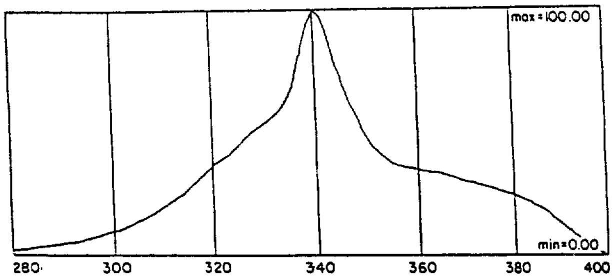


Figure 1b. Fluorescence Excitation Spectrum of the diphenylchloromethyl radical (**8**) produced by 254 nm photolysis of 0.01M solution of **7** in glassy 2-MeTHF at 77K. Emission was monitored at 520, 550, or 570 nm.

Results and Discussion

Brief photolysis (254 nm, 5 seconds) of a 0.01M solution of **7** in 2-MeTHF at 77K gives rise to only one fluorescent species. (λ_{max} emission 522 nm; λ_{max} excitation 341 nm). The fluorescence emission and excitation spectra are shown in Figure 1. We have assigned the carrier of this signal to the diphenylchloromethyl radical (**8**), whose absorption spectrum has bee reported[6], but whose fluorescence spectrum was previously unknown. The basis for this assignment rests on several factors to be discussed in detail below. If the irradiation time is increased, one sees the fomation of a second emitting species in the matrix. This second species is easily identified as diaryl carbene **9**, on the basis of the agreement of its fluorescence excitation and emission spectra with those previously reported for diphenylcarbene generated from diphenyldiazomethane.[7] It is interesting to note that two independent precursor, possessing very different ground state geometries at the central carbon atom, give rise to similar matrix fluorescence spectra both of which differ markedly from the solution phase spectrum obtained at room temperature.[8]

Table 1. Ratio of 8/9 as a function of Irradiation Time

Samle	Irradiation time* (minutes)	8/9
1.0×10^{-2}M7 in 2-MeTHF	0.5	13.2
1.0×10^{-2}M7 in 2-MeTHF	1.5	4.50
1.0×10^{-2}M7 in 2-MeTHF	3.0	2.43
1.0×10^{-2}M7 in 2-MeTHF	5.0	2.41
1.0×10^{-2}M7 in 2-MeTHF	10.0	2.20

If one monitors the ratio of (8/9) as a function of photolysis time, an interesting trend is observed. Clearly, the data, shown in Table 1, indicate that the yield of **9** relative to that of 8 increases with increasing irradiation time. We explain this observation in the following manner. Initially the only species present in the glass is **7**. Photolysis of **7** leads to photodissociative loss of a Cl atom and formation of monoradical 8. As photolysis time increased, the concentration of radical 8 increases. Secondary photolysis of 8 then forms **9** by a second photodissociation of radical 8, similar to that which initially occurred on dihalide **7**. The loss of a Cl atom from trivalent radical 8, results in the formation of the divalent diaryl carbene **9**. (Scheme 2) Thus the ratio of 8/**9** would be expected to decrease with increasing photolysis time as 8 becomes converted to **9**. In our hands the ratio of 8/**9** could not be decreased below the value of 2.20 shown in Table 1 for a **10** minute photolysis tiem. Admittedly, longer irradiation times actually led to increases in this ratio. This result may at first seem inconsistent with the proposed pathway leading to **9**. However, under the experimental conditions, **9** is both thermally and even more rapidly photochemically destroyed, thus as **9** accumulates in the matrix it too is photochemically destroyed. A possible pathway for decomposition of **9** is via H atom abstraction from the 2MeTHF matrix.[9]. Such processes are well decumented for diaryl carbenes, and in this case would lead to the diphenylmethyl radical which could go undetected due to overlapping absorption and fluorescence with 8. Thus, prolonged irradiation could lead to an increase in the ratio of 8/**9**, consistent with the proposed mechanism.

The data presented are consistent with, but do not require, the sequential nature of the double photodissociation as described in Scheme 2. The data do not exclude the possibility that **9** is simply formed concurrently with 8, by a lower quantum yield process, not involving the intermediacy of 8 at all.

Highly monochromatic laser irradiation can conceivably selectively excite one particular component of a solution or matrix, excluding all others which may be present but do not absorb significantly at the laser line. The monoradical 8 has a strong absorption band centered at 341 nm and the precursor **7** does not absorb significantly in this region. Thus using the 337 nm line of a nitrogen laser one could selectively excite 8, without depositing energy into **7**. The results of this experiment are shwon in Figure 2, where the fluorescence emission spectrum of both 8 and **9** are shwon before and after laser irradiation. Clearly, the intensity of the signal due to **9** has increased at the expense of 8 following 337 nm photolysis. One is thus compelled to conclude that monoradical 8 is indeed a photochemical precursor to **9**. This represents direct evidence supporting the stepwise nature of the double photodissociation as well as the unprecedented photolysis of a diaryl radical to a carbene.

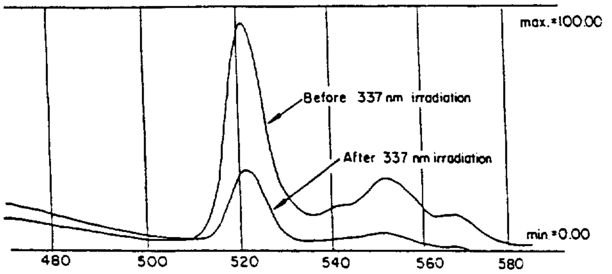


Figure 2a. Fluorescence Emission Spectrum of the diphenylchloromethyl radical (8) produced by 254 nm photolysis of 0.01M solution of **7** in glassy 2-MeTHF at 77K. Spectra shown before and after irradiation with a 337 nm laser.

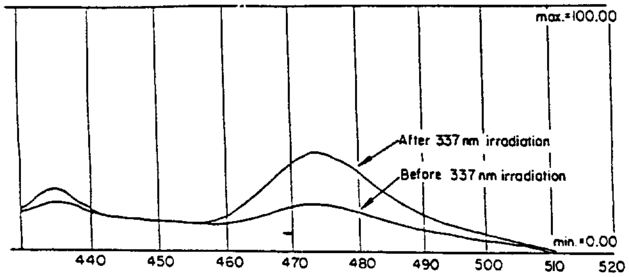


Figure 2b. Fluorescence Emission Spectrum of diphenylcarbene (**9**) produced by 254 nm photolysis of 0.01M solution of **7** in glassy 2-MeTHF at 77K. Spectra shown before and after irradiation with a 337 nm laser.

Our assignment of the diphenylchloromethyl radical 8 as the carrier of the fluorescence spectra shown in Figure 1 is crucial to the conclusions drawn above. This assignment rests on several points, and is, we feel, quite secure. First, the carrier was readily demonstrated to be a thermally unstable intermediate. Photolysis at 77K yields the emission due to 8, but warming the sample to room temperature and recooling to 77K led to the disappaearance of this emission. Furthermore, 8 is not present in samples which have not been irradiated. This excludes the possibility that 8 is a stable reaction product or fluorescent impurity present in the starting material. Second, the fluorescence excitation and emission spectra of 8 are very similar in position and appearance to those previously reported for the diphenylmethyl radical[3], and the excitation maximum agrees with the position of the absorption maximum of the diphenylchloromethyl radical.[6] The λ_{max} in the excitation spectrum of 8 is slightly blue shifted (ca. 5 nm) relative to that of the unsubstituted diphenylmethyl radical. Similar blue shifts were reported for various alkyl and aryl substituted diphenylmethyl radicals[10] In the case of the **10**-**12**, previous authors have attributed the hypsochromic shifts to an increase in the extent of twist of the phenyl groups out of the central molecular plane. This presumably results in a decrease in conjugation of the radical center over the entire π system, thus raising the energy of the first electronic transition. Our assignment of the fluorescent carrier as 8 is completely consistent with this trend. Further-

$Ph_2\dot{C}CH_3$

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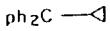

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$Ph_3C^{\cdot}$

12

more, the vibrational structure of 8 similar to that reported for radicls **10#12.**[10] The first observable vibrational line in the spectrum of 8 is 1041 cm^{-1}. Similar values were reported for **10**−**12** (1049 cm^{-1}, 1060 cm^{-1} and 1020 cm^{-1}[1,5] respectively) which the authors attributed to a C–C stretching mode. Finally, the intermediate 8 has been demonstrated to be photolabile, producing diphenylcarbene upon photolysis. We find it difficult to envision another plausible structure for 8 which could be consistent with all of the facts presented above.

In summary, 254 nm photolysis of **7** at 77K yields monoradical **8**, which was detected by its fluorescence spectrum. Monoradical **8** can be further photolyzed to **9** either by continued 254 nm irradiation, or more efficiently by laser irradiation. This represents the first case to our knowledge where a dihalide has been photolyzed to the corresponding carbene. This is possible due to the interesting photochemical properties of the intermediate radical 8, which is able to undergo photodissociation to a carbene. This procedure readily lends itself to extension into various other systems where one wishes to achieve similar goals of selective excitation.

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The ab Initio Calculation of the Spectroscopic Properties of FO and FO$^+$

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The spectroscopic properties of FO† and FO were investigated by ab initio calculation. Several different levels of theory, MP3/6-31G*, MP4/6-311G* and CISD/6-31G*, were tried and compared with experimental results of FO. In the overall performance the CISD showed the best agreement. Based on these results the spectroscopic constants of FO† are predicted.

Introduction

In the past few years the vibrational-rotational transitions of molecular ions were investigated by more improved experimental techniques[1]. The astrophysical work has shown that those molecular ions are widely distributed in the interstellar medium and has provided a great deal of information on their chemistry and dynamical conditions.

The molecular ions studied so far include CO^+,[2] HCO^+,[3,4] HN_2^+,[3] NO^+,[6] NH_4^+,[7] H_2F^+,[8]···*etc.*