of significant degradations through side reactions.

Conclusion

The results presented above show that the complete conversion of the L isomer of an α-alcohol–acid (L-lactate) can be performed with an efficiency of, at least, 97% by taking advantage of the stereospecificity of the rather cheap L-dehydrogenase and driving the system through the electrochemical regeneration of NAD^+ and the electrochemical reduction of the α-keto-acid (pyruvate). The whole process was kinetically controlled by the rate of the α-keto-acid reduction, i.e., neither by enzyme nor coenzyme deactivations. The demonstration of the feasibility of such a type of chiral inversion was our purpose. However, our study also points out a means of enhancing the productivity. Obviously, improvement implies the use of a cathode material allowing an electroactive area per volume ratio approaching that of the carbon felt. Then it would be practically conceivable to perform the anodic and cathodic reactions in the compartments of a sole reactor with configuration and size optimizations.

Experimental Section

Materials. Enzymes and biochemicals, including the lithium salts of L-lactic and D,L-lactic acids (highest purity grades available) were purchased from Sigma and used without further purification. The lyophilized L-LDH and the emulsion of D-LDH (E.C. 1.1.1.28.) were from rabbit muscle and *Lactobacillus leichmanni*, respectively. All other chemicals and the Nafion perfluorinated membranes separating the working electrode and auxiliary electrode compartments inside each reactor were from Aldrich. The felt of carbon fibers was obtained from Carbone-Lorraine.

Apparatus. The NADH concentration was determined by measuring the absorbances of solutions at 340 nm (ϵ = 6320 M^{-1} cm^{-1}) with a Perkin-Elmer 550 SE spectrophotometer. The potential of the working electrode (graphite felt) of the reactor in which NAD^+ is regenerated was controlled with a Tacussel PJT 24-1 potentiostat. The mercury pool cathode potential was controlled with a Tacussel PRT 30 01 potentiostat. The flow rates of the circulating solutions were controlled with a Gibson Minipuls 2 peristaltic pump equipped with a 4-channel head.

Reactors. The reactor in which NAD^+ was regenerated (effective area of the carbon felt anode: ca. 4500 cm^2) was as previously described[20] and was used in the vertical position, the solutions flowing from bottom to top. The reduction reactor was identical but used in the horizontal position, the carbon felt being replaced by the mercury pool (effective area ca. 15 cm^2). The two reference electrodes were connected to the exit and the entrance of the working electrode compartments of the oxidation and reduction reactors, respectively. Two channels of the peristaltic pump were used and fed with two reservoirs maintained under nitrogen atmospheres. Once the two liquid circuits of the working electrode compartments, on the one hand, and the auxiliary electrode compartments, on the other hand, were filled completely, the reservoir for the working electrode compartments initially contained always less than 2 mL. The two solutions flew, in the following order, through the oxidation reactor and through the production reactor and back to their respective reservoirs.

Procedures. In order to determine the volume of solution entrapped within the carbon felt at the end of the experiment, we compared its weight at that time to the weight of dry carbon felt introduced initially into the oxidation reactor. The data reported in Table III bear witness to the occurrence of osmosis between the two liquid circuits. The L- and D-lactate enzymatic assays were adapted from the literature.[26] They involved catalyzed oxidations in the presence of excesses of NAD^+ and hydrazine and spectrophotometric determinations of the amounts of produced NADH. The same combination of reactions was used for the assay of L-LDH enzymatically active NAD^+, excesses of L-lactate and hydrazine being then introduced. The pyruvate concentration was deduced from the increase in absorbance at 260 nm which results from the reaction of pyruvate with an excess of hydrazine. All these assays were carried out in 0.5 M carbonate buffer at pH 9.0.

Registry No. NAD, 53-84-9; NADH, 58-68-4; L-lactate, 79-33-4; D-lactic acid, 10326-41-7; L-lactate dehydrogenase, 9001-60-9; pyruvic acid, 127-17-3.

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(26) Gutmann, I.; Wahlefeld, A. W. In *Methods of Enzymatic Analysis*, 2nd ed.; Bergmeyer, H. U., Ed.; Academic Press: New York and London, 1974; Vol. 3, pp 1464–1468.

Laser Flash Photolysis of 9-Diazofluorene in Low-Temperature Glasses

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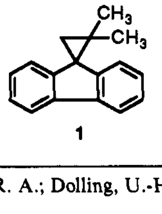
Abstract: The laser flash photolysis of 9-diazofluorene was investigated in several viscous organic glasses at low temperature. The data indicate that triplet fluorenylidene reacts with "soft warm" glasses by classical H atom abstraction, but the mechanism changes to quantum mechanical tunneling in colder and more rigid matrices.

I. Introduction

Product Studies of Carbenes in Frozen Polycrystals. Over 20 years ago Moss and Dolling[1] discovered that the chemistry of certain carbenes is tremendously sensitive to temperature. Photolysis of 9-diazofluorene (DAF) at 273 K in isobutylene, for example, generates fluorenylidene (Fl), a ground-state triplet carbene which reacts with solvent to give high yields of cyclopropane **1** and minor amounts of alkene **2**.[2,3]



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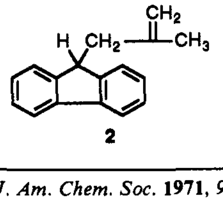

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The ratio of **1**/**2** changes only slightly between 273 and 173 K; however, at 133 K and at 77 K the product ratio is reversed. In a frozen isobutylene polycrystal the alkene product predominates and the spirocyclopropane is formed in only small quantities. In later studies Tomioka found similar changes in the product distribution in the reaction of arylcarbenes with alcohols and alkanes. These changes occur exactly at the temperature at which there is a change in phase of the solvent from a fluid solution to a frozen polycrystalline solid. Tomioka has also shown that the matrix effect on carbene chemistry applies only to those carbenes

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(1) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954.

(2) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475.

(3) For reviews see: Platz, M. S. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 143. Platz, M. S. *Acc. Chem. Res.* **1988**, *21*, 236. Wright, B. B. *Tetrahedron* **1985**, *41*, 1517.

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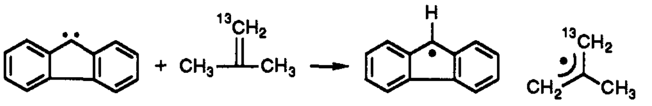
which have triplet ground states.[4]

Fluorenylidene, like many arylcarbenes, has a low-lying singlet state which has been reported to be only slightly higher in energy (~1 kcal/mol) than the triplet state.[5] This causes great complexity in mechanistic carbene chemistry. Assignment of a certain carbene reaction product to a specific spin state of the carbene is crucial to mechanistic interpretations, but it can be quite difficult to accomplish.

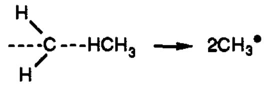
In principle, the enhanced yield of formal CH insertion product (e.g., **2**) in olefinic matrices may have a singlet or triplet origin. The matrix may change the chemistry of ^{1}Fl from cyclopropanation to C–H insertion into the allylic position of isobutylene, or the matrix environment may change the chemistry from that of ^{1}Fl to ^{3}Fl. In an elegant labeling experiment, Moss demonstrated that triplet fluorenylidene (^{3}Fl) abstracts an allylic hydrogen from isobutylene at 77 K to generate a triplet radical pair (^{3}RP). The radical pair collapses at both terminii of the allylic radical to give adduct **2** in which the label has been evenly randomized.[2]

3



A singlet insertion reaction to form **2** would bypass the radical pair and would not scramble the label. Thus, the matrix effect in isobutylene which results in enhanced yields of formal CH insertion adduct is due to an increased yield of the chemistry of triplet fluorenylidene and not due to a change in the chemistry of ^{1}Fl induced by the low-temperature matrix environment. This follows from the usual assumption that ^{1}Fl does not undergo H atom abstraction and that the triplet carbene does not undergo concerted CH insertion reactions. Very similar observations and conclusions have been reached with other arylcarbenes in various matrices.[3] The enhanced chemistry of the triplet ground state of arylcarbenes in low-temperature matrices seems intuitively reasonable. The singlet–triplet equilibrium constant K is, of course, temperature dependent, and a low temperature will dramatically reduce the equilibrium population of the low-lying singlet state. Temperature alone cannot be the whole story, however, as the change in product distribution is sharply coupled to the change in phase of the host solvent.[1-4] In this paper we present a study of the kinetics of reaction of fluorenylidene with various solvents at low temperature, and over a very wide range of viscosities. The results are consistent with our previous claims that the change in product distributions observed in matrices is a consequence of the emergence of a new reaction mechanism for hydrogen atom transfer: quantum mechanical tunneling (QMT). We will demonstrate that under conditions of high viscosity the rates of hydrogen atom abstraction reactions of the triplet ground state of the carbene are faster than can be predicted by a purely classical hydrogen atom transfer process.

EPR Studies of Carbenes in Frozen Polycrystals. Several years ago we initiated a study of the kinetics of reaction of triplet carbenes with low-temperature glasses and polycrystals using electron paramagnetic resonance (EPR) spectroscopy.[3,6] The experiments were performed by brief (30–100 s) photolysis of frozen solutions of diaryl diazomethanes between 173 and 77 K. The decay of the photogenerated carbene signal was monitored after shuttering the light source. On the basis of time-resolved experiments in deuterated and perfluorinated matrices, it was established that the EPR signal decay in protic matrices was due to hydrogen atom transfer, in accord with the earlier product studies. However, as is common with kinetic phenomena in polycrystals, the signal decay was severely nonexponential. This is usually attributed to a multiple site problem.[7] One postulates that the photogenerated triplet carbenes are formed in a multitude of nonequivalent matrix sites with respect to hydrogen atom transfer. Bauschlicher, Bender, and Schaefer have calculated the ideal transition structure geometry for the reaction of triplet methylene with methane.[8] The migrating hydrogen atom is in

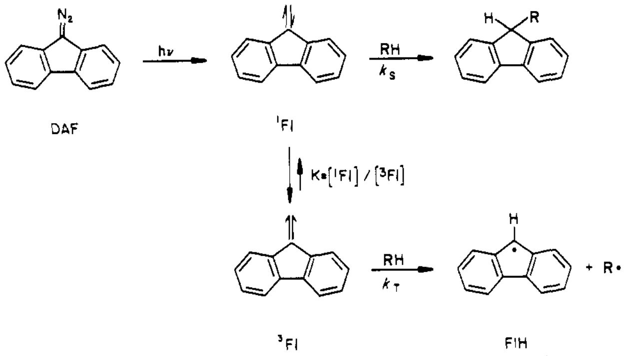


$$\text{H}_2\text{C}\cdots\text{HCH}_3 \longrightarrow 2\text{CH}_3^\bullet$$

the plane of methylene and along the line which bisects the HCH bond angle. A small variation in the direction of approach of the migrating hydrogen atom raises the energy of the reaction surface and reduces the rate of the reaction. The ensemble of photogenerated triplet carbenes detected by EPR spectroscopy exists in a multitude of local environments which differ in the orientation of the migrating H atom with respect to the carbene center. This produces the severely nonexponential kinetics which are observed.

In order to make any headway on the analysis of the complex matrix kinetics, a simplifying assumption was made.[3,6] It was assumed that the initial 20% of the EPR signal decay corresponded to a single site (of unknown orientation) and that the initial rate data could be fit to a single exponential to yield an absolute rate constant for that particular site. On the basis of kinetic isotope effects and the temperature dependence of the initial rate constants, it was concluded that the mechanism of hydrogen atom transfer was quantum mechanical tunneling (QMT). This conclusion was, of course, weakened by the assumptions used in interpreting the data. The EPR method had very limited time resolution (minutes only). The initial rate measured was the fastest resolvable matrix isolated carbene process and not the fastest site. A more serious objection to the analysis was that the fastest resolvable site at different temperatures was not necessarily the same site, thus questioning the QMT interpretation of the temperature dependence of the kinetic data. In principle, these objections could be eliminated by using a technique with time resolution superior to conventional EPR. This prompted the current study of fluorenylidene in low-temperature-glasses by laser flash photolysis. The results are largely consistent with the QMT interpretation.

Scheme I



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(4) (a) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *J. Am. Chem. Soc.* **1979**, *101*, 6009. (b) Tomioka, H.; Ozaki, Y.; Koyabu, Y.; Izawa, Y. *Tetrahedron Lett.* **1982**, *23*, 1917. (c) Tomioka, H.; Suzuki, S.; Izawa, Y. *Chem. Lett.* **1980**, 293. (d) Tomioka, H.; Ozaki, Y.; Izawa, Y. *Chem. Lett.* **1982**, 843. (e) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128. (f) Tomioka, H. *J. Am. Chem. Soc.* **1979**, *101*, 256. (g) Tomioka, H.; Miwa, T.; Suzki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753. (h) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 603. (i) Tomioka, H.; Itoh, M.; Yamakawa, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1636.

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(8) Bauschlicher, C. N., Jr.; Bender, C. F.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 3072.

Table I. Temperature Interval Over Which the Fluorenyl Radical May Be Observed upon Laser Flash Photolysis of 9-Diazafluorene

glass	temp (K)	k_{diff},[a] η[b] (temp, K)
methylcyclohexane–toluene	298–130	4.57×10^6, 6.31 (130)
methylcyclohexane-d_{14}–toluene-d_8	298–128	*c*
methylcyclohexane–methylcyclopentane	298–118	1.45×10^7, 1.80 (118)
2-methyltetrahydrofuran	298–113	1.39×10^7, 1.80 (113)
ethanol	228–153	*c*
1,2-propylene glycol	298–230	*c*
mineral oil	298–193	*c*
CCl_3F/CF_2BrCF_2Br	298–148	*c*

[a] Calculated from $k_{diff} = 8RT/(300\eta)$, where η is the viscosity in poise. Reference 13. [b] Viscosity taken from ref 14. [c] Viscosity data unavailable.

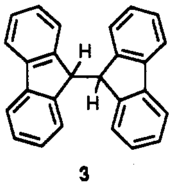
II. Temperature-Dependent Laser Flash Photolysis Studies of the 9-Fluorenyl Radical

The spectroscopy and dynamics of fluorenylidene are well developed. Laser flash photolysis of DAF generates singlet fluorenylidene (^{1}Fl) which undergoes intersystem crossing (ISC) to ^{3}Fl with a time constant of 0.25 ns at room temperature.[5] In cyclohexane, the time constant for the formation of the 9-fluorenyl radical (FlH) is 1 ns, which is also the lifetime of disappearance of ^{3}Fl. Product studies have established that singlet–triplet equilibration of fluorenylidene in alkenes is rapid relative to chemical reaction of either spin state. Although it seems probable, it remains to be similarly established whether singlet–triplet spin equilibration of Fl in alkanes is rapid at ambient temperature relative to reaction of either spin state with solvent.[9] If this condition is met, then the observed rate of decay of ^{3}Fl (or FlH formation) is given by k_{obs}, where k_s, k_t, and K are as defined in Scheme I, and

$$k_{obs} = k_t + k_sK \qquad (1)$$

Chemical analysis of the reaction products formed on photolysis of DAF in cyclohexane at ambient temperature reveals that the chemistry is largely due to that of ^{1}Fl, in which case k_{obs} is dominated by the k_sK term, assuming rapid spin equilibration.[9] As mentioned earlier, the singlet–triplet energy gap of fluorenylidene has been reported to be quite small, ~1 kcal/mol.[5] It is important to note that this is a derived quantity dependent on certain mechanistic assumptions. The magnitude of the singlet–triplet splitting has not been directly measured by spectroscopy as per methylene.[10]

Laser flash photolysis (LFP) of 9-diazofluorene in 1:1 (v/v) methylcyclohexane–toluene (MCH-T) leads to a weak transient absorption signal of the 9-fluorenyl radical. In accord with previous studies,[5] we could not resolve the rate of formation of this species by nanosecond spectroscopy. Product studies at room temperature have shown that FlH decays by dimerization to give 9,9′-bifluorenyl (3) in cyclohexane.[9] The rates of radical recombination reactions are generally close to diffusion controlled (k_{diff}).[11] Upon cooling the sample from 294 to 197 K, the yield of FlH• steadily increases. This yield is taken to be proportional to the change in absorbance (ΔOD) at 500 nm immediately after flash photolysis. Several other changes also become apparent on cooling from 294 to 197 K. The rate of radical decay slows noticeably and on the time scale of LFP stops completely on cooling the solvent (Figure 1). Lowering the temperature will, of course, greatly increase the viscosity of the sample and reduce k_{diff}. Perhaps even more striking is the fact that the yield of FlH decreases on cooling below 197 K. In fact, the radical yield is essentially zero below 130 K. Very similar results were observed in methylcyclohexane-d_{14}–toluene-d_8 glass. The pattern of first increasing and then decreasing yields of FlH with reduced temperature was repeated in 1:1 (v/v) methylcyclohexane–methylcyclopentane (MCH-MCP) and 2-methyltetrahydrofuran (2MTHF). In these glasses, however, the temperatures of disappearance of FlH were 12 to 17° cooler than in MCH-T (Table I).



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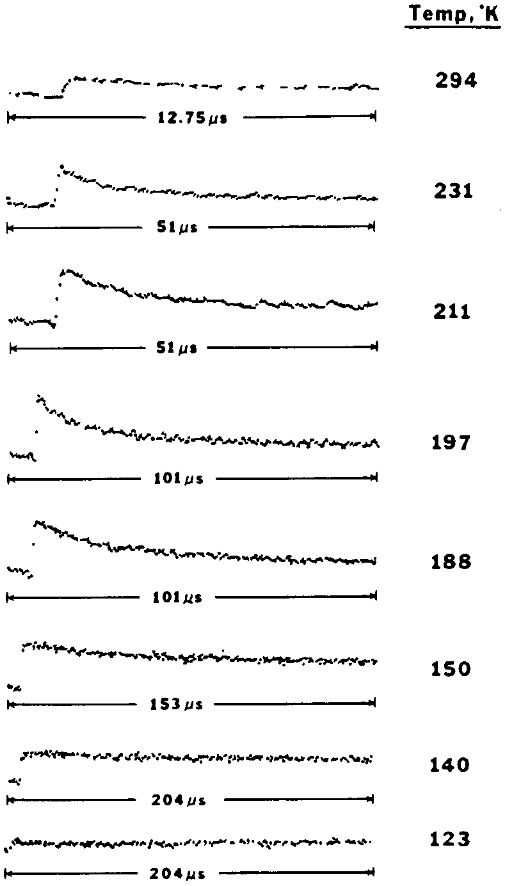

Figure 1. Decay of the 9-fluorenyl radical following laser flash photolysis measured at 500 nm.

The increased yield of FlH• on cooling from 298 to 197 K in MCH-T, MCH-MCP, and 2MTHF is easily explained as a temperature effect on the equilibrium constant K. The population of the low-lying singlet state is dramatically reduced on lowering the temperature 100° below ambient. As the temperature is lowered, the ratio of k_t/k_sK increases, resulting in an increased yield of the triplet reaction product FlH•. In other words, $E_a{}^t < E_a{}^s + \Delta H_{st}$, where E_a is the activation energy for the triplet (T) and singlet (S) reactions, respectively, and ΔH_{st} is the enthalpy separation between ^{1}Fl and ^{3}Fl.

The decreased yield of FlH as monitored by optical methods between 197 K and 130 K is due to the increased viscosity of the glass. Reaction of ^{3}Fl with solvent by hydrogen atom transfer produces a geminate triplet radical pair (^{3}RP). The components of the pair may diffuse apart to form solvent-separated radicals. It is the solvent-separated fluorenyl radicals which are detected in this experiment. Alternatively, the ^{3}RP may undergo ISC to a ^{1}RP which can then collapse without spin prohibition to form the observed reaction product (Scheme II). The rate of intersystem crossing for an average RP in solution is known from CIDNP studies to be ~10^8 s^{-1}, and this value should not be directly dependent upon temperature.[12] The value of k_{diff} is highly

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

(10) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

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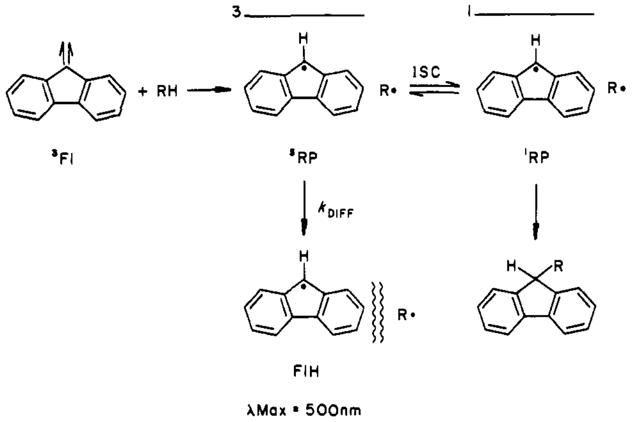
Scheme II



dependent on temperature and viscosity, η, the latter term itself a function of temperature:[13,14]

$$k_{\text{diff}} = 8RT/3000\eta \qquad (2)$$

Upon cooling MCH-T to 130 K, the value of k_{diff} has decreased to the point where none of the geminate ³RP's undergo diffusive separation. All of the ³RP's are held in the solvent cage long enough to undergo ISC to singlet radical pairs and form product (infinite cage effect). This in turn leads to no detectable signal due to FlH. Significantly, the yield of **3** (the product of diffusive separation of the radical pair) drops very sharply below 130 K, the temperature at which FlH can no longer be detected. It is interesting to note that the values of k_{diff} (see Table I) at the radical disappearance temperature in MCH-T, MCH-MCP, and 2-MTHF are quite comparable, indicating that once a critical viscosity is reached there is no diffusive separation of the radical pairs out of the solvent cage.

Under no circumstances were we able to resolve the growth of FlH. This was a major disappointment; we had hoped that sufficient lowering of the temperature would bring k_{obs} into a measurable range. This is not terribly surprising because singlet carbenes react with alkenes with negligible or even zero enthalpic barriers ($E_a^s \approx 0$).[15] If ΔH_{st} is only 1-2 kcal/mol, then k_{obs} may still be faster than the time resolution achievable with nanosecond spectroscopy at those temperatures where FlH escapes the radical cage. The combination of small FlH signal intensity and rapid rise time prevents our measuring a growth of FlH. At very low temperatures (vide infra) k_{obs} is reduced to 10^{4-6} s^{-1}, but under these conditions FlH cannot be detected because of the large cage effect.

It was previously mentioned that the rate constant of ISC from triplet to singlet RP is usually taken to be 10^8 s^{-1} from CIDNP spectroscopy. It is important to realize that this is an average value for all geminate radical pairs. In reality the RP's in solution are rapidly tumbling, and different RP's will have different orientations and separations. This is not the case for those RP's formed in a highly viscous, rigid glass at low temperature. These RP's will maintain their configuration and close proximity for time periods that are orders of magnitude longer than that of a RP in solution. We cannot detect ³RP's in rigid glasses; hence our results suggest that $k^{\text{RP}}_{\text{ts}} \geq 10^8$ s^{-1} for RP's constrained to remain in close proximity.

Scheme III

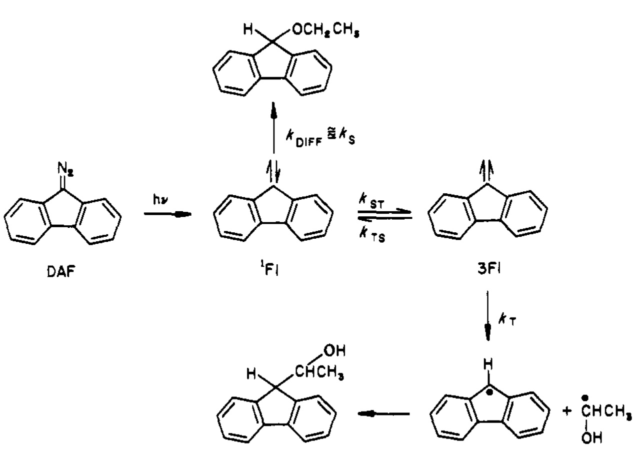
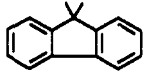


Table II. Distribution of Products Formed on Photolysis of 0.01 M DAF in Ethanol[a,b]

temp (K)	**4**	**5**	**6**
298	26	30	6
273	18	49	8
263	12	38	4
195	12	28	5
153	5	21	12
128	6	16	47
108	4	22	72
77	6	14	56

[a] Rayonet reactor with RPR 350-nm light source for 4 h. [b] Percent yields are absolute relative to dicyclohexyl internal standard, ±1%.

Laser flash photolysis of DAF in ethanol at 298 K does not give rise to a detectable signal due to FlH. This is not surprising as ¹Fl is believed to react at a diffusion-controlled rate with alcohols to give ethereal products (Scheme III). At 298 K nearly all of the nascent ¹Fl is quenched by solvent (17 M) prior to ISC (k_{ISC}) to ³Fl. However, on cooling the ethanol solution to 129 K, a signal due to FlH becomes visible. The rate of singlet to triplet carbene ISC, k_{st}, is expected to show only a minimal dependence on temperature.[16] Reduced temperature and increased viscosity will lower k_{diff} sufficiently so that $k_{\text{st}} \approx k_{\text{diff}}[\text{ethanol}]$. Under these conditions some ³Fl will be formed and will abstract hydrogen from the glass to form FlH, and, in fact, transient absorption due to FlH is observable in ethanol between 228 K and 153 K. Below the latter temperature, the absorbance disappears because the extreme rigidity of the glass prevents diffusional separation of the nascent triplet radical pair. In the rigid environment the triplet radical pair undergoes rapid intersystem crossing and collapses to form stable products. Product studies are largely consistent with this interpretation (Table II). Photolysis of DAF in ethanol at 298 K gives a 26% yield of fluorene **4**, a 30% yield of ether **5**, and a 6% yield of alcohol **6**. Alcohol **7** was observed in only trace amounts. Tomioka[17] has shown that ether **5** is photolabile in solution and fragments to form fluorene **4**. Thus the yield of insertion product derived from reaction of singlet fluorenylidene with ethanol at 298 K must be higher than 30%. The yield of formal C–H insertion product (alcohol **6**) is roughly constant between 250 and 153 K but increases sharply below this temperature. The spin state of the carbene responsible for the for-



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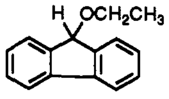

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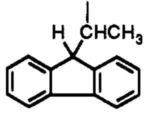

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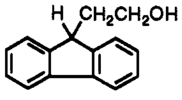

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(16) Sittzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1869.

(17) Tomioka, H.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 1070.

mation of **6** in rigid media is not known with certainty. Moss demonstrated that the enhanced yield of formal C–H insertion reaction product of Fl with isobutylene observed in a polycrystalline matrix has a triplet origin by means of a ^{13}C labeling study.[2] Reasoning by analogy suggests that the enhanced yield of the product of formal C–H insertion reaction of Fl with alcohols in matrices also has a triplet origin.[4] This cannot be proven as per isobutylene because a similar labeling study is not possible with ethanol. If product **6** does have a ^{1}Fl origin, then the matrix effect must be entirely different in alcohols than in isobutylene. If this view is correct, then the alkene matrix system exalts triplet carbene chemistry whereas an alcohol matrix must for unknown reasons change ^{1}Fl chemistry from OH to C–H insertion. In the interest of economy a single type of matrix effect has been preferred in the literature, and compounds such as **6** have been attributed to triplet carbene chemistry.

Laser flash photolysis of DAF in 1,2-propylene glycol (PG) gives results comparable to those observed in mineral oil. Unlike the study in ethanol, the fluorenyl radical can be observed following laser flash photolysis of DAF in PG. Cooling to 230 K results in the disappearance of the FlH absorption. The data in PG at room temperature resemble those in ethanol at 228 K. At 228 K the signal in PG is gone. The differences observed in the kinetics of FlH in PG and ethanol are due to their very different viscosities at the same temperature.

The laser flash photolysis of DAF was also studied in a perhalogenated glass of 1:1 CCl_3F–CF_2BrCF_2Br.[18] It has been reported that Fl abstracts chlorine atoms from carbon tetrachloride at rates near diffusion control.[5] Transient absorption at 500 nm was observed and assigned to a 9-halo fluorenyl radical formed by abstraction of either a chlorine or a bromine atom of the solvent in analogy to the earlier report. CIDNP studies of Roth have demonstrated that both singlet and triplet methylene can abstract chlorine atoms from carbon tetrachloride; thus it is not clear whether the halogenated radical is formed from singlet or triplet fluorenylidene.[19] The 9-halo fluorenyl radical can be observed between 298 K and 148 K.

III. Temperature-Dependent Laser Flash Photolysis Studies of Triplet Fluorenylidene: Results

The 9-fluorenyl radical can be detected by its transient absorbance (λ_{max} = 500 nm), over a range of temperature which depends upon the particular glass. Under no circumstances were we able to simultaneously observe FlH and triplet fluorenylidene (λ_{max} = 470 nm) at the same temperature. We were able to observe ^{3}Fl by laser flash photolysis of glasses cooled 5–10° below the temperature at which the signal of FlH disappeared.

Table III. Pseudo-First-Order Rate Constants for ^{3}Fl Decay in MCH-T

temp (K)	k (s^{-1})	viscosity (P)	k_{diff} (M^{-1} s^{-1})[a]
122	$(6.42 \pm 0.20) \times 10^5$	1.00×10^2	2.70×10^5
120	$(6.15 \pm 0.12) \times 10^5$	1.58×10^2	1.68×10^5
115	$(5.21 \pm 0.09) \times 10^5$	1.00×10^3	2.55×10^4
110	$(1.37 \pm 0.03) \times 10^5$	7.94×10^4	3.07×10^3
109	$(7.93 \pm 0.10) \times 10^4$	1.26×10^5	1.92×10^2
106	$(5.42 \pm 0.10) \times 10^4$	6.31×10^5	37.2
105	$(2.49 \pm 0.03) \times 10^4$	1.00×10^6	23.2
101	$(5.89 \pm 0.12) \times 10^3$	1.26×10^7	1.78
99	$(3.72 \pm 0.13) \times 10^3$	1.00×10^8	0.22
93	$(3.12 \pm 0.10) \times 10^3$	5.01×10^9	4.11×10^{-3}
90	$(2.53 \pm 0.17) \times 10^3$	1.00×10^{11}	1.99×10^{-4}

[a] The values of k_{diff} for the reaction of ^{3}Fl with MCH-T can be converted to a pseudo-first-order rate constand (and compared directly with k, s^{-1}) by multiplication by 10*M*, the approximate molarity of the glass.

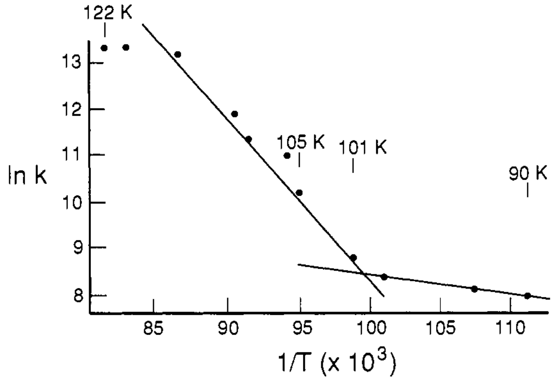
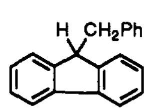


Figure 2. Arrhenius plot of the pseudo-first-order decay of ^{3}Fl in methylcyclohexane–toluene (k in s^{-1}, T in K).

Methylcyclohexane–Toluene. In this matrix the disappearance of the radical signal occurs at 130 K, and triplet decay was measurable from 122 K to 110 K. The pseudo-first-order rate constants range from 6.4×10^5 to 2.5×10^3 s^{-1} within this temperature interval. A complete list of rate constants is presented in Table III, along with the corresponding Arrhenius plot in Figure 2. The rate constants of this work are reported as ±1 standard deviation. The linear decrease of the observed pseudo-first-order decay rates versus $1/T$ deviates at ca. 105 K, producing a clear break in the plot. Above the break, the average calculated activation energy (E_a) is 5.5 kcal/mol with a log (A/s^{-1}) value of 15.8 (Table IV). By comparison, literature values for the decay of triplet diphenylcarbene in solution are E_a = 3 kcal/mol and log (A/M^{-1} s^{-1}) = 8.[20] For ^{3}Fl decay below the break, the Arrhenius parameters fall to E_a = 1.2 kcal/mol and log (A/s^{-1}) = 6.2. Platz and Senthilnathan found an E_a value of 1.5 but a much lower log (A/s^{-1}) value of ~1 for ^{3}Fl decay in polycrystalline toluene between 77 and 88 K using EPR spectroscopy.[6] The large difference in log (A) values observed in the EPR and laser flash work is responsible for the difference in carbene lifetimes measured by the two techniques. The lifetimes determined by EPR (Table V) are several orders of magnitude longer than those observed by laser flash photolysis. This demonstrates that the EPR studies focused upon the small percentage of carbenes which were very long lived and ignored the more rapidly decaying carbenes present in the matrix.

Product studies confirm that ^{3}Fl reacts with glassy MCH-T to give high yields of formal CH insertion products (Table VI). Photolysis of 0.01 M DAF in 1:1 methylcyclohexane–toluene at 77–110 K gives nearly quantitative yields of insertion products **8** and **9**. Thus, we feel confident in relating k_{obs} with the reaction



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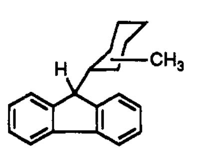

9

of spin equilibrated fluorenylidene with the matrix by either ^{3}Fl abstraction (k_t) or by ^{1}Fl insertion (k_sK). We prefer to equate k_{obs} with k_t under matrix conditions primarily due to Moss's results with fluorenylidene in labeled isobutylene. This is in contrast to solution phase studies where we have equated k_{obs} with k_sK on the basis of product studies[5b] and isotopic labeling.[9]

Between 105 K and 90 K the viscosity of MCH-T glass increases by five orders of magnitude (Table III).[14] It is obvious that dramatically increasing the viscosity of the glass influences the kinetics of the carbene disappearance. One might expect that increased viscosity would decrease the rate of all second-order processes by reducing molecular rotational correlation times τ_c and k_{diff}, thereby depressing the rate at which a pair of reacting molecules can achieve the desired transition structure orientation. This is not the effect which is observed; increased viscosity in hydrocarbon glasses *increases* the rate relative to the values predicted by extrapolation of the Arrhenius data obtained at higher

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(18) Grimson, A.; Simpson, G. A. *J. Phys. Chem.* **1968**, *72*, 1776.

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

(20) (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. *Chem. Phys. Lett.* **1984**, *105*, 539. (c) Barcus, R. A.; Platz, M. S.; Scaiano, J. C. *J. Phys. Chem.* **1987**, *91*, 695.

Table IV. Arrhenius Parameters for the Pseudo-First-Order Decay of Triplet Fluorenylidene

	high temperature			low temperature		
glass	range (K)	log (A/s^{-1})	E_a (kcal/mol)	range (K)	log (A/s^{-1})	E_a (kcal/mol)
MCH-T[a]	122–101[e]	15.8	5.5	101–90[g]	6.2	1.2
E[b]	143–123[f]	16.4	7.0	123–95[g]	5.0	0.7
PG[c]	222–189[f]	12.9	7.9	185–165[g]	5.1	1.3
2MTHF[d]	109–96[g]	18.9	6.4	96–87[g]	12.0	3.5
CCl_3F/CF_2BrCF_2Br	136–106[h]	8.7	1.9	106–87[g]	9.1	2.1

[a] Methylcyclohexane–toluene. [b] Ethanol. [c] 1,2-Propanediol. [d] 2-Methyltetrahydrofuran. [e] 8 data points. [f] 5 data points. [g] 4 data points. [h] 6 data points.

Table V. Calculated and Observed EPR Rate Constants at 77 K

glass	k(calc), s^{-1} [a]	k(obs), s^{-1} [b]
MCH-T	4.1×10^2	$3.6 \pm 0.8 \times 10^{-3}$
E	1.6	$7.4 \pm 0.9 \times 10^{-3}$
PG	27	$3.1 \pm 0.1 \times 10^{-4}$ $3.06 \pm 0.4 \times 10^{-4}$
2MTHF	3.3×10^2	$7.4 \pm 0.8 \times 10^{-3}$
$CFCl_3/CF_2BrCF_2Br$	1.5×10^3	*c*

[a] Calculated from the low-temperature regime of the laser flash photolysis data of Table IV. [b] Observed by EPR. Samples were irradiated with a 1000-W Hg-Xw arc lamp through a $CuSO_4$ filter for 100 s. The concentration of DAF was 0.01 M. [c] No EPR signal of ^{3}Fl was observed.

Table VI. Distribution of Products Formed on Photolysis of 0.01 M DAF in MCH-T[a] and MCH-T-D[b]

matrix[c,d]	T (K)	**4**	**3**	**8**	**9**
H	150	6	26	16	19
H	130	3	20	17	38
H	123	3	3	27	33
H	110	0	0	60	40
H	95	0	0	65	35
H	77	0	0	61	37
D	150	2	10	10	19
D	130	1	18	14	30
D	123	0	0	20	28
D	110	0	0	49	49
D	95	0	0	49	27
D	77	0	0	42	32

[a] Methylcyclohexane–toluene. [b] Methylcyclohexane-d_{14}–toluene-d_8. [c] Rayonet reactor with 350-nm light source for 4 h. [d] Percent yields are absolute relative to dicyclohexyl internal standard, ±1%.

temperatures. Using the Arrhenius parameters found for MCH-T between 122 K and 105 K, one would predict a pseudo-first-order rate constant of 1.6×10^1 s^{-1} at 90 K. This is more than 100 times slower than the observed rate. In MCH-T the rapid onset of the rigidity of the glass accelerates carbene decay relative to the value expected by simple extrapolation of the temperature, assuming no change in viscosity. Above 110 K the values of k_{obs} are very close to k_{diff}, while below this temperature k_{obs} is much larger than k_{diff}. In fact, at 90 K k_{obs} is 10^6-fold larger than k_{diff}. The fact that $k_{obs} \gg k_{diff}$ indicates that the hydrogen atom transfer process is best thought of as an intra- rather than an intermolecular process, and the carbene and the hydrogen donor form a single kinetic unit.

The rotational correlation time τ_c can be calculated from the equation:[21]

$$\tau_c = 4\pi\eta a^3/3kT \qquad (3)$$

where k is Boltzmann's constant and a is the radius of rotation of fluorenylidene, which we have arbitrarily chosen as shown below.

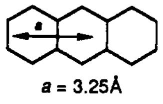

Table VII. Calculated Rotational Correlation Times and Measured Lifetimes of Fluorenylidene in MCH-T

temp (K)	τ_c (s)[a]	τ_{obs} (s)[b]
90	1.16×10^{-3}	3.95×10^{-4}
105	9.92×10^{-3}	4.02×10^{-5}
120	1.37×10^{-6}	1.56×10^{-6}

[a] Calculated from eq 3. [b] Experimental value ($=1/k_{obs}$) of Table III.

Table VIII. Pseudo-First-Order Rate Constants for ^{3}Fl Decay in 2-Methyltetrahydrofuran

temp, K	k, s^{-1}	viscosity, P
109	$(8.70 \pm 0.10) \times 10^5$	1.03×10^2
106	$(6.49 \pm 0.11) \times 10^5$	2.81×10^2
99	$(5.89 \pm 0.28) \times 10^4$	1.26×10^5
96	$(1.84 \pm 0.08) \times 10^4$	1.58×10^6
95	$(9.13 \pm 0.10) \times 10^3$	3.16×10^6
92	$(7.29 \pm 0.26) \times 10^3$	1.00×10^8
87	$(2.29 \pm 0.10) \times 10^3$	2.24×10^{10}

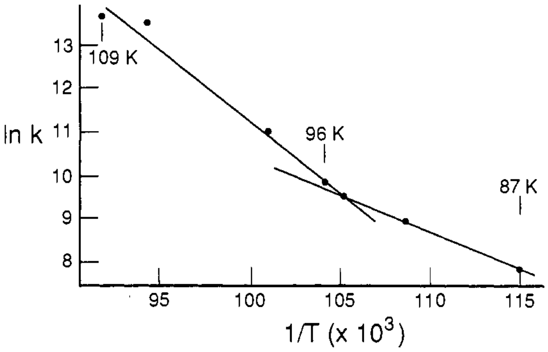

Figure 3. Arrhenius plot of the pseudo-first-order decay of ^{3}Fl in 2-MTHF (k in s^{-1}, T in K).

The size of a has been calculated from the geometry of fluorene determined by X-ray crystallography.[22] It is instructive to compare (Table VII) the calculated values of τ_c in MCH-T with the observed lifetimes τ_{obs} ($=1/k_{obs}$ of Table III). At 90 K the calculated rotational correlation time is more than a million times longer than the lifetime of ^{3}Fl. Under these conditions of temperature and viscosity, we view the reaction as a hydrogen atom migrating from a static molecule of the glass to a static carbene molecule. The rate of this process can exceed k_{diff} because it does not require diffusional or rotational motion of either the carbene or the donor. At 105 K τ_c is still much greater than τ_{obs}, and the reaction is best viewed as an intramolecular process in which carbene and matrix H atom donor define a single kinetic unit. At 120 K, τ_c and τ_{obs} are comparable, and the calculated value of k_{diff} is similar to k_{obs}. At and above 120 K it is likely that the reaction of ^{3}Fl with the glass is best described as an intermolecular process.

2-Methyltetrahydrofuran. The decay of ^{3}Fl could be measured between 109 and 87 K in glassy 2-MTHF. The data are listed in Table VIII; the viscosity data are again taken from Greenspan and Fischer.[14] The Arrhenius plot is shown in Figure 3. The

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(21) Carrington, A. R.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper and Row, New York, 1967; p 189.

(22) Belskii, V. K.; Zavodnik, V. E.; Vozzhennikov, V. M. *Acta Cryst.* **1984**, *C40*, 1210.

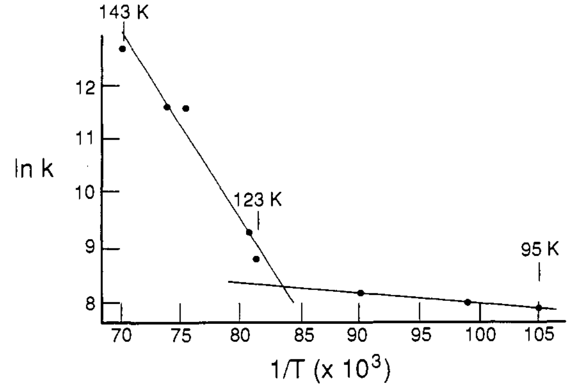

Figure 4. Arrhenius plot of the pseudo-first-order decay of ^{3}Fl in ethanol (k in s^{-1}, T in K).

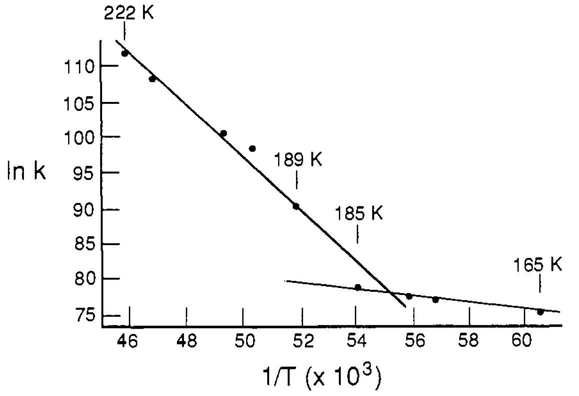

Figure 5. Arrhenius plot of the pseudo-first-order decay of ^{3}Fl in 1,2 propylene glycol (k in s^{-1}, T in K).

decay rates of ^{3}Fl in 2-MTHF were also measured by EPR (Table V). The kinetics in 2-MTHF are more rapid than in MCH-T. At 109 K the decay of ^{3}Fl in 2-MTHF is 10-fold larger than in MCH-T at the same temperature. We feel that this rate enhancement factor originates from both the different intrinsic hydrogen atom donating abilities of the glasses as well as from their viscosities. The viscosity of MCH-T is about 10^3 times larger than the viscosity of 2-MTHF at 109 K. The Arrhenius plot of the 2-MTHF data is clearly nonlinear. The break in the MCH-T plot occurs near 99 K where $\eta = 10^8$ poise (P). The break in the 2-MTHF data occurs near 92 K where η again equals 10^8 P. This demonstrates that the change in the kinetics of carbene decay can be clearly associated with a critical viscosity of the glass.

Ethanol and Propylene Glycol. The decay of ^{3}Fl could be measured in ethanol and in PG. The associated Arrhenius plots are shown in Figures 4 and 5. Once again the plots are nonlinear. The decay rates at low temperature are much faster than predicted by extrapolation of the data obtained at higher temperatures. The break temperatures observed in ethanol and PG are 123 and 187 K which are much higher than in MCH-T and 2-MTHF. We suspect that the alcohol glasses become very viscous at relatively high temperatures (the actual viscosities of these glasses as a function of temperature are unknown). This is quite plausible for PG which is rather viscous even at room temperature.

Methylcyclohexane-d_{14}–Toluene-d_8. Laser flash photolysis of 9-diazofluorene in MCH-d_{14}-T-d_8 gave ^{3}Fl which decayed at measurable rates between 130 and 88 K. The kinetics observed in MCH-d_{14}-T-d_8 were severely nonexponential, quite unlike the data obtained in the hydrocarbon glasses which could be fit to a simple exponential. It was possible to fit the initial 20% of the signal decay to an exponential expression as in our EPR work.[6] This approach gave initial "rate constants" which were of the same order of magnitude as those observed in MCH-T. An Arrhenius plot of the initial rate constants measured in MCH-d_{14}-T-d_8 is very similar to those observed in MCH-T (Figure 2). The small KIE's observed at these rather low temperatures are inconsistent with triplet H atom abstraction (either classical or by QMT) or even with ^{1}Fl insertion.[9] The small kinetic isotope effects (KIE's) measured are understandable when combined with product analysis. Photolysis of 9-diazofluorene in MCH-T-d below 100 K (the break point in Figure 2, MCH-T-H) gives lower yields of adducts **8** and **9** than in methylcyclohexane–toluene and higher yields of unreacted diazofluorene (Table VI). Thus, one cannot claim that k_{obs} of ^{3}Fl in the deuterated glass (below 100 K) can be cleanly associated with the reaction of fluorenylidene with the matrix. Thus, the apparently small values of k_H/k_D observed below 100 K are without significance since we have not actually measured k_D for the reaction of fluorenylidene with the glass. Above 100 K (the break point in Figure 2), the total product yields in the proton and deuterated matrices are indistinguishable. We have previously reported that ^{3}Fl is photosensitive.[23] Photolysis of ^{3}Fl in diethyl ether or toluene matrices at 77 K promotes H (or D) atom abstraction to produce RP's which can be detected by EPR. It seems likely then that the adducts formed between Fl and the deuterated matrix at 77 K result from *photochemical* rather than thermal reactions of ^{3}Fl. At first glance it seems inconsistent that we can detect the RP product of ^{3}Fl reaction by EPR but not by LFP. This is not really the case though because the RP spectra observed previously by EPR are clearly formed by secondary photolysis rather than by thermal reactions of ^{3}Fl. In the LFP experiment we are only monitoring for RP's produced by thermal reactions of the carbene. It is important to note that we can detect RP's produced by thermal reactions of triplet dibenzocycloheptadienylidene at 77 K by EPR.[23] This is not possible with fluorenylidene derived RP's because they themselves are unstable under these conditions.[23]

Table IX. Pseudo-First-Order Rate Constants for ^{3}Fl Decay on CCl_3F/CF_2BrCF_2Br

temp, K	k, s^{-1}
136	$(4.82 \pm 0.37) \times 10^5$
131	$(3.55 \pm 0.27) \times 10^5$
118	$(1.82 \pm 0.18) \times 10^5$
114	$(1.24 \pm 0.08) \times 10^5$
110	$(1.01 \pm 0.08) \times 10^5$
106	$(6.39 \pm 0.32) \times 10^4$
103	$(3.97 \pm 0.16) \times 10^4$
100	$(2.33 \pm 0.15) \times 10^4$
87	$(6.46 \pm 1.14) \times 10^3$

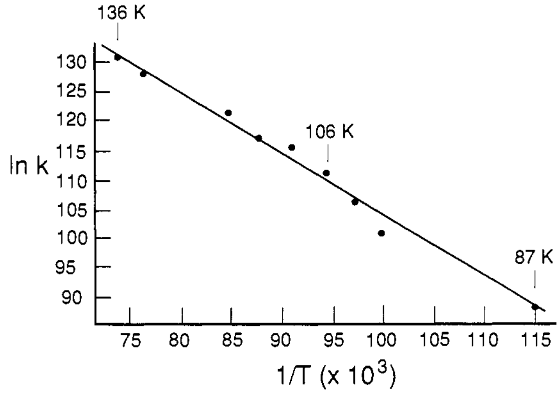

Figure 6. Arrhenius plot of the pseudo-first-order decay of ^{3}Fl in 1:1 $CFCl_3/CF_2BrCF_2Br$ (k in s^{-1}, T in K).

Perhalogenated Glass. Laser flash photolysis of 9-diazofluorene in 1:1 $CFCl_3$–CF_2BrCF_2Br gave ^{3}Fl which decayed at measurable rates between 136 and 87 K (Table IX). The viscosity of this glass as a function of temperature is not known, but these samples appeared far more fluid at low temperatures than the hydrogen-containing glasses. The data gave a good fit to a simple first-order rate law at all temperatures. We expect that the mode of ^{3}Fl decay in this glass is by Cl and Br atom abstraction. The Arrhenius plot is shown in Figure 6. Unlike all of the hydro-

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[23] Barcus, R. A.; Wright, B. B.; Leyva, E.; Platz, M. S. *J. Phys. Chem.* **1987**, *91*, 6677.

gen-containing glasses studied in this work, the plot is reasonably linear over the entire temperature range. If there is any curvature in the plot it is in the direction *opposite* to that observed in hydrogen-containing glasses; the decay of ^{3}Fl in $CFCl_3/CF_2BrCF_2Br$ at low temperature is somewhat slower than that predicted by extrapolation of the data obtained at higher temperature, which is in accord with chemical intuition.

IV. Discussion

It has been assumed that a rapid spin-state equilibrium exists between ^{1}Fl and ^{3}Fl, in which case the observed decay kinetics are a composite of the elementary reaction rates arising from both spin states, and may be expressed by eq 1, where $K = [^1\mathrm{Fl}]/[^3\mathrm{Fl}]$. Using the estimated upper limit of 2 kcal/mol for the $S-T$ free energy gap reported by Griller, Platz, and Scaiano,[5b] and assuming that $\Delta H_{ST} \approx \Delta G_{ST}$, the derived lower limit of the value of K may be estimated at a given temperature. Upon assigning k_s the value of the diffusion-controlled limit, rough guesses of k_s, K and k_T may be made. At 122 K, the highest temperature and the softest glass for which triplet decay was measured in methylcyclohexane–toluene (and where the reaction may perhaps still be thought of as intermolecular), K may be calculated from eq 4, assuming ΔG is still close to 2 kcal/mol at 122 K.

$$\Delta G = -RT \ln (K) \qquad (4)$$

$$K = 9.1 \times 10^{-5}$$

The value of k_{diff} in MCH-T at 122 K is 2.7×10^5 M^{-1} s^{-1},[13,14] which may be multiplied by 10*M* (the approximate molarity of the glass) to obtain an approximate pseudo-first-order rate constant for a diffusion-controlled process. As $k_s \leq k_{diff}$, one may immediately discern that, if this treatment is valid, the contribution of the k_sK term to k_{obs} is vanishingly small. Repeating the procedure but setting the value of the $S-T$ gap at 1 kcal/mol, as preferred by Schuster, gives $k_t = 6.27 \times 10^5$ s^{-1}, which still indicates a minimal influence of the k_sK term on k_{obs} at this temperature.

$$6.42 \times 10^5 = k_t + [(2.70 \times 10^6\ \mathrm{s^{-1}})(9.1 \times 10^{-5})] \qquad (5)$$

$$6.42 \times 10^5 = k_t + 2.46 \times 10^2$$

$$k_t \approx k_{obs}$$

$$6.42 \times 10^5 = k_t + [(2.70 \times 10^6\ \mathrm{s^{-1}})(5.5 \times 10^{-3})] \qquad (6)$$

At still lower temperatures, K will decrease sharply and the equilibrium population of ^{1}Fl will be negligible; however, at lower temperatures it is no longer valid to think of the reaction as intermolecular and to assume that $k_s \leq k_{diff}$. The assumption of rapid singlet–triplet spin equilibration is more safely applied to glasses than solution-phase studies. Singlet to triplet carbene ISC will not vary substantially with temperature.[16] Thus, even if ^{1}Fl reacts with the glass at a diffusion-controlled rate ($k_{diff} \approx 10^5$ M^{-1} s^{-1}, 120 K relatively warm, soft glass), this is much too slow to compete with intersystem crossing ($k_{isc} \approx 10^{10}$ s^{-1}).

The broken Arrhenius plots of Figures 2–5 demand comment. The simplest explanation is a change in the reaction mechanism from a classical H atom abstraction at high temperature to a QMT controlled abstraction at low temperatures. The shapes of Figures 2–5 are exactly what one would predict for such a change in mechanism.[24] The only reaction of ^{3}Fl we can imagine which might be hundreds of fold more reactive in a rigid glass than in a fluid solution is reaction of ^{3}Fl with nitrogen to regenerate DAF. This is perhaps the mechanism of ^{3}Fl decay in deuterated and perhalogenated matrices. Are the broken Arrhenius plots of Figures 2–5 signalling a change in mechanism from reaction of ^{3}Fl with the matrix to reaction with nitrogen? We think not because a linear Arrhenius plot (Figure 6) is observed in a perhalogenated glass, where QMT is impossible but reaction with N_2 is still available. Do the breaks in the Arrhenius plots of Figures 2–5 signal a change in mechanism from reaction of ^{3}Fl to ^{1}Fl? We reject this interpretation for three reasons. First, it contradicts the isotopic labeling study of Moss.[2] Secondly, we do not see how a cold rigid environment will accelerate singlet CH bond insertion processes. Finally, the population of ^{1}Fl is vanishing small below the break temperature.

The most decisive evidence in favor of QMT would, of course, be provided by the temperature-dependent kinetic isotope effects. Unfortunately, the chemistry of fluorenylidene in rigid perdeuterated glasses is complex and does not involve thermally activated deuterium atom abstraction; thus one cannot associate k_{obs} with this reaction. Furthermore, recent EPR studies of Barcus[23] indicate that various ground state triplet carbenes undergo a change in mechanism between protic and deuterated matrices. The carbenes decay by hydrogen atom abstraction reactions of their ground triplet states in protic glasses but decay by photochemical reactions only in perdeuterated matrices.[23] Thus, it is likely that the formal CD insertion products listed in Table III are not derived from D atom abstraction of the ground triplet state.

V. Conclusions

Previous interpretations of the decay kinetics of triplet carbenes in H atom donating matrices attributed to quantum mechanical tunneling are consistent with the present study. Multiple site problems are even more severe than originally suspected. The EPR method focused on only a small subset of the carbene decay corresponding to the least reactive sites in the matrix. The apparently low isotope effects reported earlier, which were attributed to the multiple site problem, are now more properly recognized as a result of a change in decay mechanisms between protic and deuterated glasses.

Reaction parameters above the break appear to mimic those found in solution-phase work. The Fl activation energies measured above the break in the Arrhenius plots in all of the glasses studied are comparable to those of DPC measured in solution phase.[20] The higher reactivity of ^{3}Fl relative to ^{3}DPC is a consequence of higher log (A) values. Quantum mechanical tunneling of hydrogen does not become important in glassy media until the glass is cooled to a critical temperature and viscosity.

VI. Experimental Section

9-Diazofluorene (9-DAF) was prepared by a literature procedure.[1,2] Methylcyclohexane, methylcyclopentane, and toluene were purified by stirring with concentrated H_2SO_4, washing with distilled water, and distilling over calcium hydride. 2-Methyltetrahydrofuran was purified by distillation over calcium hydride. Ethyl alcohol and propylene glycol were obtained as spectroscopic grade (Aldrich) and used without further purification. Trichlorofluoromethane and 1,2-dibromotetrafluoroethane were purchased from Fluorochem Ltd. and used as received. Methylcyclohexane-d_{14} and toluene-d_8 were purchased from MSD Isotopes in 99+% isotopic purity.

In a typical experiment, 9-DAF was dissolved in a small volume of the solvent of choice to create a concentrated stock solution. Stock solutions were then diluted to 1×10^{-3} M or until the resulting solution exhibited an absorbance of 1.0–1.2 at 308 nm for excimer laser photolysis. Solutions to be photolyzed were placed in cells made from suprasil tubing which was fashioned into cells containing a 1-cm^2 base. Samples were deaerated by bubbling with oxygen-free nitrogen immediately prior to use. Samples were placed in a double-walled cylindrical copper jacket containing ports for the laser and monitoring beams. A coil of tubing between the walls carries the flow of cooling nitrogen gas. The cylinder was enclosed by a glass sheath containing optical windows that were aligned with the beam ports. Two rings of styrofoam between the cylinder and sheath provided a dead air space and insulation. Cooling of the sample was accomplished by flowing precooled nitrogen gas.

To prevent excessive localized bleaching of sample solutions in a liquid state, the sample cell was shaken following data collection at two to three temperatures. Once solutions were glassy, localized bleaching was prevented by sliding the sample cell up the cell holder until the laser pulse struck a fresh region of the glass. When no unphotolyzed region of the sample remained, the cell was removed and thawed to room temperature, shaken, and given several minutes to re-equilibrate after being returned to the cell holder.

Product mixtures were analyzed with a Hewlett Packard 5830A gas chromatograph using a 6 ft by $^1/_8$ in. 10% SE-30 column. Solutions for analysis were sealed in 4-mm Pyrex tubes which had been prewashed with

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[24] Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980.

ammonium hydroxide and oven dried. Samples were photolyzed at 350 ± 30 nm using two Southern New England ultraviolet RPR 3500 bulbs. All EPR measurements were performed with a Varian E-112 spectrometer. The kinetic protocols have been described.[6]

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Registry No. 9-DAF, 832-80-4; CCl_3F, 75-69-4; CF_2BrCF_2Br, 124-73-2; D_2, 7782-39-0; fluorenylidene, 2762-16-5; 9-fluorenyl, 2299-68-5; methylcyclohexane, 108-87-2; toluene, 108-88-3; 2-methyltetrahydrofuran, 96-47-9; ethanol, 64-17-5; propylene glycol, 57-55-6; methylcyclohexane-d_{14}, 10120-28-2; toluene-d_8, 2037-26-5; methylcyclopentane, 96-37-7.

Changes of the Carbonyl Stretching Spectra with Temperature

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Abstract: It is shown that the apparent collapse or coalescence of carbonyl stretching bands of η^4-norbornadiene tricarbonyl iron can be attributed to thermal motion of the carbonyls in *one* potential well. This explanation is in contrast to explanations involving motion between wells. The one-well explanation is also consistent with the expected time scales for all of the possible motions.

I. Introduction

In a number of recent papers, the infrared spectra of the tricarbonyl (η^4-norbornadiene) iron (**1**) has been reported.[1-3] The carbonyl stretching bands appear to broaden and shift together ("collapse"), and at high enough temperature, the collapsed bands appear to narrow. All of this is reminiscent of the behavior of nuclear magnetic resonance (NMR) bands in systems undergoing chemical exchange, and so the infrared spectra are interpreted analogously.

We have, however, argued that vibrational spectra cannot be interpreted in this manner because of the many order of magnitude difference between the magnetic resonance and vibrational time scales.[4-6]

The exchange process for **1** is an internal rotation (Figure 1) in which the three CO groups rotate against the framework formed by the iron and the norbornadiene group. This framework has two symmetry planes, and the axial CO lines up with one of them. The other two CO groups are equatorial and do not line up with a symmetry element of the norbornadiene. A rotation of $2\pi/6$ brings one of the equatorial CO groups to the axial position.

The time scale of the motion required to collapse the bands can be characterized by the splitting between the bands of the interchanging groups, that is about 10 cm^{-1} in the infrared and 10 Hz in the NMR. The infrared splitting corresponds to a time, $t = 2\pi c\bar{\nu}$, for the splitting in wavenumbers (with c the speed of light) of 1.9 ps. The NMR splitting corresponds to a time of $1/2\pi\nu$ or 16 ms. The internal rotation over a barrier is much faster than the NMR time, but slower—or at best the same order of magnitude—than the required infrared time.

η^4-Diene tricarbonyls with low symmetry such as the η^4-butadiene $Fe(CO)_3$ have activation barriers of about 9 kcal/mol and so show no special phenomena in the infrared.[3] In contrast, the η^4-bornadiene and η^4-cyclobutadiene complexes are thought to have barriers of only about 1-1.5 kcal/mol and show collapsing bands in the infrared.[3]

The low barriers make for large torsional displacements of the carbonyl groups, displacements that increase with temperature. These increasing displacements have the effect of moving certain bands in the spectrum toward one another as the temperature increases, and this is just the effect that has been observed. No jump from axial to equatorial need be present.

II. Results and Discussion

A. Band Shifts in the Isotopically Pure Compounds. The exchange of the tricarbonyls occurs by an internal rotation of the carbonyl groups—a motion often described as a turnstile rotation. The effect of the rotation on the spectra can be discussed using our previous treatment[6] of similar effects in the C–H stretching bands of the methyl group at the end of n-alkane chains. We follow our previous notation in the following. We start with the isotopically pure tricarbonyls (that is, $X(C^{12}O^{16})_3$) and write the carbonyl Hamiltonian as

$$H_v = \tfrac{1}{2}\sum_{i=1}^{3} G^{-1}\dot{r}_i^2 + \tfrac{1}{2}\sum_{i=1}^{3} F r_i^2 + \tfrac{1}{2}\sum_{i}^{3}\sum_{j}^{3} f r_i r_j \qquad (1)$$

The r_i are the C=O stretching coordinates, F is the diagonal force constant, and f is the off-diagonal force constant. The kinetic energy matrix element, G^{-1}, is given by $\mu_C + \mu_O$. μ_A is the reciprocal of the mass of the A atom. This vibrational Hamiltonian is for three identical carbonyls—we add the effect of the diene framework separately. The vibrational Hamiltonian is not quite complete, since coupling to the other degrees of freedom is not included. Possible force fields for C–O stretches have been much discussed,[7,8] and better approximations are available if necessary.

We add the interaction with the diene framework with a Hamiltonian

$$H_{VT} = \tfrac{1}{2}\sum_{n=1}^{\infty}\sum_{i=1}^{3}\delta_n \cos\left\{n\left(\theta + (i-1)\frac{2\pi}{3}\right)\right\} r_i^2 \qquad (2)$$

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