$\nu_{C'_{Gly2}}$. Torchia and Lyerla[16] do observe this order in the random coil polypeptide poly($Gly_1$-$Gly_2$-$Pro_3$-$Gly_4$) (see Table I).

Peptide residues with $\gamma$ substituents in their side chain, such as Val, Leu, Asp, Glu, Met, etc., will generally have carbonyl $^{13}C$ chemical shifts upfield from the C′ resonances in Ala due to the additional $\gamma$ effects incurred through $\chi_1$ rotations (see Figure 2) about their $C^\alpha$–$C^\beta$ side chain bonds.[13–15] Several more examples of the residue and sequence dependencies of the carbonyl $^{13}C$ chemical shifts in random coil polypeptides are presented in Table I.

Aside from the possibility of intra-side-chain $\gamma$ interactions in those residues with long side chains (His, Tyr, Glu, Met, Arg, Orn, Lys, etc.), the side chain $\beta$ carbon is involved in $\gamma$ interactions with the C′, O, and N atoms of its own and the succeeding peptide bond. The backbone rotations $\phi$ and $\psi$ (see Figure 2) determine whether or not the $C^\beta$ carbon is gauche to the atoms of these peptide bonds. When $\phi_i = 0, 240°$ $C^\beta{}_i$ is $\gamma$ gauche to $C'_{i-1}$; when $\psi_i = 0, 120°$ $C^\beta{}_i$ is $\gamma$ gauche to $N_{i+1}$; and when $\psi_i = 180, 300°$ $C^\beta{}_i$ is $\gamma$ gauche to $O_i$. It is evident that the $^{13}C$ chemical shift of a residue's side chain $\beta$ carbon should reflect the residue's backbone conformation ($\phi$,$\psi$) via the $\gamma$ gauche effect.

As an example, in the conformational transition of a polypeptide from the $\alpha$-helical to the random-coil state, ($\phi$,$\psi$) change from $\approx$120°,120° (right-handed $\alpha$-helix) to all the low-energy values encompassed by the usual ($\phi$,$\psi$) conformational energy map[10] of a randomly coiling peptide residue. From the probabilities[11] that $\psi = 0, 120, 180, 300°$ obtained from the conformational energy map appropriate to a randomly coiling peptide residue with a $\beta$-$CH_2$ group in its side chain,[10] it is possible to estimate[20] that the expected difference in the chemical shift of the side chain $\beta$ carbon in the $\alpha$-helix and the random-coil states is $\Delta\nu_{C^\beta}$($\alpha$-helix − random coil) $\approx 0.6(\gamma_{C^\beta,N} - \gamma_{C^\beta,O})$.

From $^{13}C$ NMR studies of carbon- and nitrogen-substituted alkanes, as described by Stothers,[7] it is apparent that $\gamma_{C,N}$ is significantly larger than $\gamma_{C,O}$. Clearly then we would expect a downfield shift of the $C^\beta$ side chain resonance on passing from the $\alpha$-helical to the random-coil conformation.

Such a downfield shift in the $^{13}C$ NMR resonance of $C^\beta$ is observed[21–23] upon disrupting the $\alpha$-helical polypeptide conformation and passing to the random coil, regardless of whether or not temperature, pH, or salt concentration is the perturbing influence which unwinds the $\alpha$-helix. The carbonyl carbon $^{13}C$ NMR chemical shift is not a suitable indicator of the peptide residue conformation in the $\alpha$-helix to random-coil transition, because the state of the carbonyl oxygen (hydrogen bonded, solvated, or not) also strongly effects the chemical shift of this carbon.

When an L-Pro residue[24] succeeds an amino acid residue with a $\beta$-$CH_2$ or $CH_3$ group, such as L-Ala, the conformation about the $C^\alpha$–C′ bond in the residue preceding L-Pro is restricted[10] to $\psi \approx 300°$, while $\phi$ rotations are unimpeded by the succeeding L-Pro residue. Consequently, the difference in chemical shifts expected at $C^\beta{}_{L\text{-}Ala}$ in the randomly coiling polypeptide sequences –L-Ala-X– and –L-Ala-L-Pro–, where X is not L-Pro, is $\Delta\nu_{C^\beta L\text{-}Ala}$ (–L-Ala-L-Pro- - -L-Ala-X–) $\approx 0.4(\gamma_{C^\beta,N} - \gamma_{C^\beta,O})$. Since $\gamma_{C^\beta,N} > \gamma_{C^\beta,O}$ we expect $\nu_{C^\beta L\text{-}Ala}$ in –L-Ala-L-Pro– to come upfield from the resonance position in –L-Ala-X–. This expectation is confirmed by the $^{13}C$ chemical shifts reported in ppm downfield from $Me_4Si$ for $C^\beta{}_{L\text{-}Ala}$ in *tert*-butoxycarbonyl-L-Ala-L-Pro,[17] 16.95 ($Me_2SO$) and 15.55 ($D_2O$), and in –Gly-Gly-L-Ala-L-Ala,[13,19] 18.2 ($Me_2SO$) and 17.7 ($D_2O$).

Based on the examples discussed in this report, it seems reasonable to conclude that substituent effects (principally $\gamma$ substituents) on the $^{13}C$ NMR chemical shifts of the backbone carbonyl and side chain $\beta$ carbons can be utilized to understand the microstructure of polypeptides. Even though the quantitative details remain to be established, the relative $^{13}C$ chemical shifts of backbone carbonyl and side chain $\beta$ carbons already provide us with a means to determine the residue sequence and conformations of polypeptide chains.

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# Determination of the Absolute Rates of Decay of Arylcarbenes in Various Low Temperature Matrices by Electron Spin Resonance Spectroscopy

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*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.* *Received April 11, 1980*

**Abstract:** The absolute decay rates of diphenylcarbene and fluorenylidene have been measured by ESR. The decay is pseudo first order and arises from reaction of the carbene with the glassy or crystalline host. The kinetics are sensitive to the chemical nature of the matrix, the viscosity of the matrix, the concentration of the diazo precursor, and the history of the sample with respect to photolysis. The signal decay is nonexponential due to site problems in the matrix. The decay can be fitted to either a $t^{1/2}$ or $t^{1/3}$ vs. log $I$ dependence. The predominant carbene decay pathway is by hydrogen atom tunneling through a small barrier. This is indicated by very low Arrhenius parameters and anomalous isotope effects. The kinetic study explains the predominance of hydrogen atom abstraction–recombination products observed by other workers.

The chemistry and spectroscopy of arylcarbenes have been exhaustively studied.[2] The solution chemistry of these species is best interpreted by two reactive states, a very reactive stereoselective singlet and the less reactive, less stereoselective triplet.[3]

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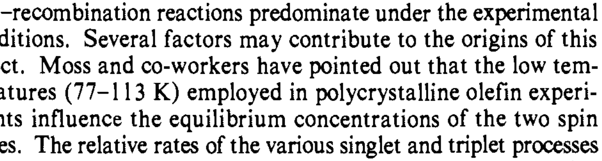
Low temperature matrix isolation ESR spectroscopy has convincingly demonstrated the triplet ground-state multiplicity of arylcarbenes.[4]

In recent years several studies concerned with the reactions of arylcarbenes in solid matrices have appeared.[5,6] The results have consistently shown that triplet carbene hydrogen atom abstraction–recombination reactions predominate under the experimental conditions. Several factors may contribute to the origins of this effect. Moss and co-workers have pointed out that the low temperatures (77–113 K) employed in polycrystalline olefin experiments influence the equilibrium concentrations of the two spin states. The relative rates of the various singlet and triplet processes will also change with temperature according to their respective Arrhenius parameters.[5] This interpretation is supported primarily by the linear dependence of the logarithm of the carbene product ratios vs. temperature$^{-1}$.

Tomioka has invoked matrix effects to interpret the reactions of carbenes in alcohol and alkane matrices. The solid matrix must severely restrict the range of motion available to the arylcarbene.[6] The product mixture also reflects the "packing" and the "hardness" of the matrix.

To gain further insight into the nature of arylcarbene processes in matrices, we have undertaken the measurement of their absolute decay rates in various systems. In contrast to the wealth of theoretical, spectroscopic, and chemical data accumulated on carbenes, there have been very few direct kinetic studies of the species. Hutchinson and Doetschmann prepared a mixed crystal of diphenyldiazomethane (**2**) in 1,1-diphenylethylene.[7] Photolysis of the crystal at low temperature produced triplet diphenylcarbene (**1**) which was detected by ESR. The Arrhenius parameters for reaction of **1** with each component of the host were determined by the decay of the ESR signal.



3

1

$\log A = 5.6\ s^{-1}$
$E_a = 4.6$ kcal/mol

$\log A = 14.8\ s^{-1}$
$E_a = 7.8$ kcal/mol

The only report of solution-phase carbene kinetics is the flash photolysis study of Closs and Rabinow.[8] These workers measured the dimerization of triplet **1** in benzene and the cycloaddition of the carbene with butadiene in the same solvent. In this case the carbene was monitored by optical spectroscopy.

The triplet ESR spectrum of **1** has been observed in several organic crystals and glasses at 77 K, but no quantitative lifetime estimates were known at the outset of this work.[9] The results demonstrate that by suitable choice of diazo concentration, host, and temperature, the lifetimes of arylcarbenes can be brought into a convenient range for routine kinetic analysis.

## Results and Discussion

The spectral splittings (500–2000 G) observed in triplet ESR spectroscopy originate from dipole–dipole interactions between the two unpaired electrons.[10] High viscosity of the medium prevents rapid tumbling of the triplet and averaging of the dipolar interaction.[11] The averaging process must be suppressed or it will narrow the triplet spectrum to a featureless line that is difficult to assign. This complicates the choice of solvent and temperature which can be employed for rate studies. The matrix must be soft enough to permit diffusion and bimolecular chemistry, but hard enough to preserve the integrity of the spectrum.

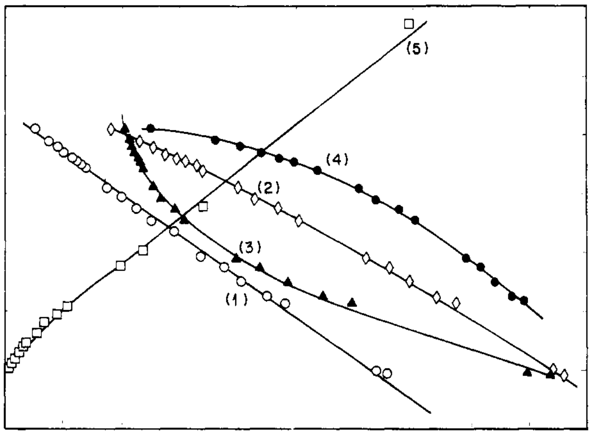
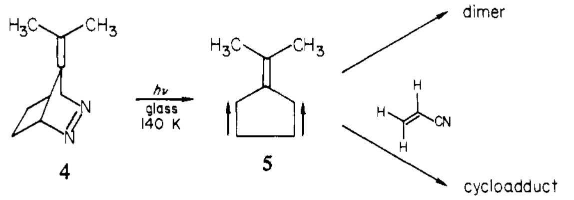


Figure 1. Plots of (1) log $I$ vs. $t^{1/2}$, (2) log $I$ vs. $t^{1/3}$, (3) log $I$ vs. $t$, (4) log $I$ vs. log $t$, (5) $1/I$ vs. $t$ for diphenylcarbene in 2:3 (iso)propanols (1- and 2-) at −175 °C with $I_0 = 65$ and $I_\infty = 18$ (arbitrary units) at the end of 60 min.

Platz and Berson found suitable temperature and viscosity conditions for the study of triplet biradical reactions by ESR.[12] Irradiation of azo compound **4** in a glassy mixture of 2 parts of 1-propanol to 3 parts of 2-propanol (propanolic glass) at 140 K produces the triplet spectrum of **5**. The glassy spectrum is identical with that obtained at 4 K in the solid state; hence it has not been narrowed by molecular motion. The spectrum decays rapidly when irradiation is discontinued. The decay is second order, indicative of dimerization, but changes to pseudo first order in the presence of acrylonitrile. The kinetics are in good agreement with a wealth of chemical evidence.[13]



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**Kinetics of Diphenylcarbene in Glasses.** The irradiation of 0.189 M diphenyldiazomethane (**2**) in propanolic glass at 140 K does not produce a measurable carbene signal. The sample must be cooled by approximately 40 K in order to observe triplet **1**. Under these conditions the signal decays at a convenient rate when the irradiation is discontinued. The temperature–viscosity window in which kinetics can be conveniently performed is quite narrow (~10°). At lower temperatures the signal decays extremely slowly; at higher temperatures it is not observed.[14]

Several temperature–viscosity windows were found to be suitable for kinetics in organic glasses containing 10% **2** (by volume): 2-methyltetrahydrofuran (2MTHF), 2MTHF–alcohols, me-

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(14) A referee has suggested "that loss of epr signal at 1100 gauss may not be due to a decrease in triplet concentration but simply due to an increase in motion of the triplet which would broaden the line and make it appear as if there were less triplet present". This interpretation can be ruled out as the line shape of the EPR signal is the same at the beginning and toward the end of every kinetic run. Hence there is no large change in triplet rotational correlation time during the reaction. Furthermore, the triplet line shape in glasses (at temperatures greater than 77 K) is identical with the line shape observed in hexafluorobenzene polycrystals at 77 K. The triplet carbene is extremely stable under these conditions.

thylcyclohexane–toluene (MCH–T), MCH–methylcyclopentane (MCP), MCH–isopentane (IP) (2.5% **2**), and methanol–ethanol (2.5% **2**). A plot of the logarithm of the signal intensity (log $I$) vs. time ($t$), for the decay of **1** in propanols, significantly deviates from linearity even at short reaction times. In every system studied the apparent reaction rate decreases during the course of the reaction. This would be expected for a second-order reaction; however, $I^{-1}$ does not plot against $t$ either (see Figure 1).

The decay might consist of competing second-order and pseudo-first-order decay, but there are several objections to this interpretation. First, similar nonlinearity is observed in each of the glasses studied. If the mixed-order kinetics explanation is correct, the competition between dimerization and reaction with solvent must be comparable in each glass studied. In a mixed-order kinetics scenario, the reaction will be predominantly second order at the initial, high concentrations of **1**. The initial carbene decay does indeed give a reasonable fit to pure second-order kinetics (see Figure 1). Taking the upper limit of the triplet concentration as $10^{-4}$ M gives an initial dimerization rate constant of $2.1 \times 10^{1}$ $M^{-1}$ $s^{-1}$ in propanolic glass at 98 K. The calculated diffusion-controlled rate constant in propanolic glass at 98 K is $2.72 \times 10^{-3}$ $M^{-1}$ $s^{-1}$.[15] The predicted first half-life of decay is $>10^{6}$ s, which is nearly four orders of magnitude slower than that which is observed (~420 s). The observed reaction rate is substantially faster than a diffusion-controlled carbene dimerization. To interpret the matrix reactions as due to dimerization requires that the addition of 0.189 M **2** to propanolic glasses lowers the viscosity of the medium by more than $10^{4}$ P.[16]

The data make more sense when it is considered as a diffusion-controlled pseudo-first-order reaction of the carbene with the matrix. If the matrix concentration is 10 M, this model predicts a first half-life of $\tau_{1/2} = 0.69/[(2.72 \times 10^{-3}\ M^{-1}\ s^{-1})(10\ M)] = 26$ s. Unlike the calculated dimerization rate constant which is faster than the diffusion rate, the calculated pseudo-first-order rate constant is roughly 20 times slower than the upper limit of reactivity. Considering the error in the viscosity of the glass (containing 2.5% **2**), the theoretical model for diffusion-controlled reactions, and the nonexponential triplet decay, the observed half-life is in fair agreement with the anticipated diffusion-controlled value. Finally the pseudo-first-order kinetics interpretation agrees with the findings of both Moss and Tomioka. These workers found insignificant amounts of dimeric product (tetraphenylethylene) in their matrix studies.[5,6]

Nonexponential decay of radicals in matrices has been observed many times.[17] The phenomenon has been explained by different sites in the matrix. The reactivity of the radical or the carbene will depend on its fixed orientation relative to the host. In the early stages of the reaction the reactive carbene sites are quickly depleted. The remaining carbenes are in less reactive sites; hence the apparent pseudo-first-order rate constant decreases. It was empirically determined that log $I$ vs. $t^{1/2}$ in propanolic glass gives excellent linear plots. This observation is not fortuitous: all of the glassy matrix triplet decays give excellent log $I$ vs. $t^{1/2}$ plots over 80% of the triplet decay. Consequently the pseudo-first-order rate constants of Table I are reported in units of $s^{-1/2}$. We are unaware of any existing theoretical justification for this treatment. However, this type of kinetic behavior has been seen before in matrix reaction systems.[18]

The pseudo-first-order decay of triplet **1** in 2-MTHF at 89 K is 0.035 $s^{-1/2}$ (Table I). To obtain a similar decay rate in a 1:1 mixture of 2-MTHF–$CH_3OH$, one has to raise the reaction temperature by over 10 K. From this one might conclude that **1** is intrinsically more reactive with 2-MTHF than methanol, but examination of other glasses reveals problems with this reasoning. Triplet **1** is roughly 50% more reactive in 1:1 ethanol–methanol than in 2-MTHF at 92 K, implying that ethanol is much more reactive toward **1** than either 2-MTHF or methanol. However, the decay rates of **1** in 1:1 2-MTHF–ethanol and pure 2-MTHF are virtually identical. Obviously one cannot make simple comparisons of reactivity between various glasses on the basis of their H atom donating ability and solution kinetics. The viscosity of the glass can have more effect on the absolute reactivity of the carbene than its chemical nature. Furthermore, due to poor solubility, the concentration of **2** in 1:1 methanol–ethanol is only 2.5% by volume, as compared with a 10% volume of **2** in 2-MTHF–alcohols. The kinetics of **1** in various glasses is strongly influenced by **2**, and will be discussed later in more detail.

Table I. Pseudo-First Order Rate Constants of Diphenylcarbene in Organic Glasses Containing 10% Diphenyldiazomethane[a]

| solvent system | temp, K | $k$, $s^{-1/2}$ $\times 10^{3}$ |
|---|---|---|
| 2-methyltetrahydrofuran (2-MTHF) | 92 | 44 ± 4.0 |
| | 89 | 35 ± 3.0 |
| 1:1 $CH_3OH$-2-methyltetrahydrofuran (2-MTHF) | 99 | 32 ± 3.0 |
| | 96 | 30 ± 3.0 |
| 1:1 $C_2H_5OH$–2-MTHF | 96 | 58 ± 2.0 |
| | 92 | 46 ± 0.5 |
| | 88 | 23 ± 0.4 |
| 1:1 1-propanol–2-MTHF | 96 | 39 ± 1.2 |
| | 92 | 32 ± 1.3 |
| | 88 | 25 ± 1.3 |
| 1:1 benzyl alcohol (BzOH)–2-MTHF | 115 | 39 ± 3.0 |
| | 112 | 18 ± 2.0 |
| 1:1 methylcyclohexane (MCH)–toluene (T) | 111 | 46 ± 4.0 |
| | 108 | 30 ± 2.0 |
| | 105 | 25 ± 2.0 |
| 1:1 MCH–methylcyclopentane (MCP) (2.5% diazo) | 118 | 18 ± 1.5 |
| | 114 | 14 ± 1.2 |
| | 111 | 9 ± 0.7 |
| 1:1 $CH_3OH$–$C_2H_5OH$ (2.5% diazo) | 95 | 96 |
| | 92 | 65 |
| | 89 | 58 |
| 1:3 MCH–isopentane (IP) (2.5% diazo) | 154 | 18 |
| 15% cyclohexadiene in 1:3 MCH–(IP) | 112 | 29.1 |

[a] Rate constants are obtained from the plot of log $I$ vs. $t^{1/2}$ for Tables I–VI.

The viscosities of several organic glasses have been measured as a function of temperature,[16] and undoubtedly change as a solute is added. However, for the purposes of discussion we will assume that the relative viscosities of glasses containing diazo compound **2** are similar to the relative viscosities of the pure materials. The viscosity of pure 1:1 ethanol–methanol is $10^{4}$ times greater than that of 2-MTHF at 92 K.[16] Since the respective decay rates of **1** in these glasses are within an order of magnitude, the data imply that the intrinsic reactivity of the alcohols toward the carbene must be much greater than that of the ether, in a classical low viscosity solution sense. The viscosity of 2-MTHF–methanol is not known and cannot be readily extrapolated from the data available. The kinetic results require that adding alcohols to 2-MTHF increases the viscosity if one insists on a classical low viscosity solution argument.

Other disagreements with chemical intuition are present in Table I. Benzylic hydrogens are excellent hydrogen atom donors, yet the decay of triplet **1** is faster in $CH_3OH$–2-MTHF than in benzyl alcohol(BZOH)–2-MTHF. As the mole fraction of benzyl alcohol in 2-MTHF is increased, the carbene decay actually slows down. To obtain similar rate constants the benzyl alcohol study must be run at 16 K higher temperature than pure 2-MTHF. Triplet **1** in methylcyclohexane–toluene (1:1) is much less reactive than in 2-MTHF. The toluene-containing glass must be warmed by 20 K relative to 2-MTHF to obtain comparable rate constants. These must surely be matrix effects rather than chemical ones.

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(15) The diffusion controlled rate constant is calculated from $k = 8RT/(3000n)$ where $R = 8.31 \times 10^{7}$ erg/(mol K) and $n$ is the viscosity in poise.[16] Caldin, E. F., "Fast Reactions in Solution"; Wiley: New York, 1964.

(16) The viscosity of propanolic glass at 98 K is $10^{10}$ P. Greenspan, H.; Fischer, E. *J. Phys. Chem.* **1965**, *69*, 2466–2469.

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Table II. Matrix Arrhenius Parameters for the Decay of 1 in Organic Glasses Containing 10% 2

| solvent systems | log $A$, $s^{-1/2}$ | activation energy, $E_a$, cals/mol |
|---|---|---|
| 1:1 $CH_3OH$-2-MTHF | −1.464 ± 0.04 | 470 ± 40 |
| 1:1 $C_2H_5OH$-2-MTHF | 2.137 ± 0.25 | 1934 ± 150 |
| 1:1 propanol-2-MTHF | −0.328 ± 0.05 | 920 ± 70 |
| 1:1 benzyl alcohol-2-MTHF | 6.674 ± 0.61 | 4811 ± 380 |
| 1:1 MCH-toluene | 2.206 ± 0.26 | 2323 ± 190 |
| 1:1 MCH-MCP | 2.030 ± 0.24 | 2595 ± 210 |
| 2-MTHF | 0.690 ± 0.14 | 1291 ± 100 |

The triplet carbenes seem more reactive in matrices containing many accessible, abstractable hydrogens (e.g., alkyl alcohols) than in matrices containing relatively few reactive hydrogens (e.g., benzyl alcohol) per molecule.

The temperature dependence of the ESR signal decay was studied in the accessible kinetics window. The narrow temperature range (less than 15 K in optimal cases) precluded accurate determination of the Arrhenius parameters; hence the data of Table II must be taken as only rough estimates. The imprecision is particularly bad for the log $A$ values as these are based on the slope of two or three narrowly spaced points extrapolated to a distant intercept. Measurement of the slope is more precise than that of the intercept; hence the $E_a$ values are on somewhat firmer ground than that of log $A$. Raising the reaction temperature will also increase the observed rate constant by decreasing the viscosity. This can change the decay rates substantially if the reaction occurs at close to the diffusion rate. Thus, the Arrhenius parameters may incorporate the viscosity temperature dependence. Caution must be exercised in interpreting the Arrhenius parameters, but it is fair to say that the values measured in the glass are much smaller than those expected for solution reactions.

The very low log $A$ and $E_a$ values obtained are striking but consistent with the effect of the matrix on the kinetics. The very low frequency factors imply that bringing the reactants together in the correct orientation is unlikely in a viscous media. These observations are again well precedented. Campion and Williams observed that the activation energy for reaction of methyl radicals with methanol was 0.9 kcal/mol in a viscous alcoholic glass, whereas the solution value was 8.2 kcal/mol.[19,20] The log $A$ value observed in the low temperature reaction was 0.041 $s^{-1}$. The solution phase log $A$ value is estimated to be 14 $s^{-1}$ for this reaction.[19]

$$\cdot CH_3 + CH_3OH \rightarrow CH_4 + \cdot CH_2OH$$

Williams has interpreted the change in Arrhenius parameters with temperature and phase as due to a change in mechanism. As the reaction temperature is lowered the classical reaction rate decreases, and eventually becomes much slower than decay by hydrogen atom tunneling. The hydrogen atom tunneling interpretation seems appropriate for the reactions of triplet **1** studied herein. It nicely accounts for the domination of hydrogen atom abstraction–recombination chemistry observed from triplet carbenes at low temperature.

Table III. Pseudo-First-Order Rate Constants of Diphenylcarbene in Organic Glasses Containing Low Concentrations of Diphenyldiazomethane

| solvent system | temp, K | $k$, $s^{-1/2}$ × $10^3$ | concn, M × $10^3$ |
|---|---|---|---|
| 1:1 $CH_3OH$-2-MTHF | 89 | 51 ± 2.0 | 203.6 |
| 1:1 $C_2H_5OH$-2-MTHF | 89 | 39 ± 3.0 | 162.0 |
| 1:1 1-propanol-2-MTHF | 89 | 39 ± 4.0 | 197.0 |
| 1:1 2-propanol-2-MTHF | 89 | 41 ± 3.0 | 245.0 |
| 2:3 propanols (1- and 2-) | 98 | 35 ± 3.0 | 189.0 |
| 2:1 BzOH-2-MTHF[a] | 116 | 24 | 161.0 |
|  | 111 | 21 | 161.0 |
| 1:1 BzOH-2-MTHF | 111 | 25 ± 2.0 | 194.0 |
| 1:2 BzOH-2-MTHF | 101 | 38 | 185.0 |
|  | 97 | 22 | 185.0 |
| 1:1 MCH-toluene | 98 | 29 ± 3.0 | 164.0 |
| 2-MTHF | 89 | 79 ± 6.0 | 119.0 |
| 1:1 cyclohexene-2-MTHF | 77 | 15 ± 0.8 | 106.0 |
| 1:1 1,3-cyclohexadiene-2-MTHF | 77 | 21 ± 2.0 | 129.0 |
| 1:1 $CH_3OH$-$C_2H_5OH$ | 89 | 32 | 155 |
|  | 77 | 12 | 155 |
| 1:3 MCH-IP | 134 | 19 | 17 |

[a] The data for this system give a better plot when considered as log $I$ vs. $t^{-1/3}$. This treatment gives $k$ = 0.050 and 0.048 $s^{-1/3}$ at 116 and 111 K, respectively.

The Arrhenius parameters are calculated from matrix rate constants which are in units of $M^{-1}$ and $s^{-1/2}$. The second-order rate constants are obtained by dividing the pseudo-first-order rate constants by 10 M. This assumes that the solvent concentration is 10 M. It is a rough guess because the respective solvent contraction data are not known for the glasses employed. However, this assumption probably adds less error to the calculated Arrhenius parameters than the narrow temperature range of the study. To test whether the matrix rate constants ($M^{-1}$ $s^{-1/2}$) give anomalously low Arrhenius parameters, the initial decay of **1** (~30%) in 1:1 ethanol–2-MTHF was fitted to simple pseudo-first-order kinetics. If the Arrhenius parameters are recalculated on the basis of these initial rate constants, $E_a$ changes from 1934 to 2838 cal/mol and log $A$ changes from 2.137 to 3.780 $s^{-1}$. The conventional parameters are still extremely low compared with the anticipated solution phase values, and still support a hydrogen atom tunneling mechanism.

The decay of triplet **1** in 1:3 methylcyclohexane–isopentane containing 2.5% diphenyldiazomethane proceeds at an exceptionally high temperature. These samples are not transparent when cooled to low temperature, implying that the sample is no longer a uniform glass and its viscosity is much higher than that of the pure binary solvent. Microcrystals of **2** may also be present. To test this possibility [**2**] was lowered to less than 1%. Repetition of the kinetic analysis on the low concentration sample revealed a large change in reactivity. Whereas the kinetics were performed at 154 K and 2.5% **2**, it was necessary to lower the temperature to 134 K to monitor the low concentration sample (see Table III). Drastically lowering the concentration of **2** in the binary solvent lowers the viscosity of the glass and produces a uniform sample. The carbene can now be generated in sites containing abstractable solvent hydrogen atoms rather than inert **2**.

The concentration of **1** was reduced in the other solvent systems. In every example studied, a large decrease in **2** led to an increase in reactivity of the carbene. Much smaller changes in diazo concentration have little effect on the decay kinetics. The pseudo-first-order rate constants of **1** in 1:1 $CH_3OH$–2-MTHF at 89 K are 0.049, 0.051, and 0.051 $s^{-1/2}$ at 0.2036, 0.1018, and 0.0509 M diazo compound **2**, respectively. The Arrhenius parameters observed in glasses containing low concentrations of **2** are still extremely low. For example, in 1:2 benzyl alcohol–2-MTHF (0.185 M) $E_a$ = 1255 cal/mol and log $A$ = −0.223 $s^{-1/2}$. The low values are not matrix artifacts. If the initial triplet decay in 1:1 ethanol–2-MTHF (0.155 M **2**) is fitted to simple first-order kinetics, the recalculated conventional Arrhenius parameters are only $E_a$ = 2838 cal/mol and log $A$ = 3.78 $s^{-1}$, as compared with the matrix parameters $E_a$ = 1120 cal/mol and log $A$ = 1.238 $s^{-1/2}$. The dilution effects suggest that triplet **1** is not decaying by reaction with diazo precursor. This is consistent with the work of Moss and Tomioka who found small yields of azine **3** in their matrix reactions.[5,6]

The decay kinetics of **1** are sensitive to the history of the sample with respect to photolysis. The kinetics are performed by briefly

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(19) Campion, A.; Williams, F. *J. Am. Chem. Soc.* **1972**, *94*, 7633–7637; see also ref (18).

(20) (a) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1972**, *94*, 2930–2934. (b) Le Roy, R. J.; Sprague, E. D.; Williams, F. *J. Phys. Chem.* **1972**, *76*, 546–551.

Table IV. Effect of Sample History with Respect to Photolysis on the Decay of 1 in Propanolic Glass at 98 K

| without melting the sample | | with melting the sample | |
|---|---|---|---|
| runs | $k$, $s^{-1/2} \times 10^3$ | runs | $k$, $s^{-1/2} \times 10^3$ |
| 1 | 35 | 1 | 35 |
| 2 | 30 | 2 | 37 |
| 3 | 28 | 3 | 34 |
| 4 | 27 | 4 | 37 |
| 5 | 25 | | |

Table V. Arrhenius Parameters and Rate Constants of Decay of Fluorenylidene in Organic Glasses[a]

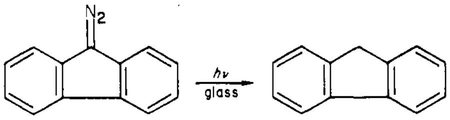
| solvent system | temp, K | $k$, $s^{-1/2}$ $\times 10^3$ | log $A$ | $E_a$, cal/mol |
|---|---|---|---|---|
| 2:3 propanols | 88 | 42 ± 3.4 | −1.55 ± 0.04 | 334 ± 27 |
| (1- and 2-) | 77 | 32 ± 2.6 | | |
| 1:1 BZ OH/2- | 84 | 32 ± 2.6 | −1.99 ± 0.08 | 195 ± 16 |
| MTHF | 77 | 24 ± 2.0 | | |
| 2-MTHF | 77 | 38 ± 3.0 | | |

[a] Concentration of 6 between 0.1 and 0.2 M.

irradiating the sample to build up the triplet signal. When the photolysis is discontinued, the decay of the signal is measured. One can repeat the experiment in either of two ways: (a) simply reirradiate the frozen sample or (b) thaw the sample, recool to a glass, and then irradiate. The two procedures give slightly different results (see Table IV). If procedure (a) is followed, then the pseudo-first-order rate constants are found to systematically decrease, although the quality of the log $I$ vs. $t^{1/2}$ plots remains constant. In the latter procedure the rate constants do not change. Photolysis of **2** to produce the carbene, with its subsequent formation of reaction products, causes local disturbances in the glass. This results in higher local viscosities, a depletion of reactive sites and lower rate constants. By thawing the glass after each kinetic run, the small amounts of reaction products formed are homogeneously distributed. Upon recooling, the bulk properties of the glass have been recovered. The data reported in all of the tables were measured in the latter fashion. The reproducibility of the data is good.

The sample photolysis history effect can be illustrated in another experiment. If a 0.161 M solution of **2** in 1:2 benzyl alcohol-2-MTHF is irradiated for 30 s, a relatively small triplet signal is observed. The pseudo-first order decay rate constant is 0.036 $s^{-1/2}$. When this tube is thawed, recooled, and reirradiated for 240 s, the initial triplet concentration is twice that observed previously. However, the decay rate constant observed is appreciably smaller in the latter (long photolysis time) system, only 0.028 $s^{-1/2}$ as the most reactive sites were depleted during photolysis. All of the data reported in all of the tables were determined after 30-s photolysis. If triplet **1** was decaying by dimerization, then doubling the initial triplet concentration should increase the decay rate by a factor of 4. This behavior was not observed, and further strengthens the interpretation of the decay of **1** as due to reaction with the matrix.

**Kinetics of Fluorenylidene with Organic Glasses.** The reactions of fluorenylidene **6** were studied and compared with that of diphenylcarbene. Triplet **6** was generated by photolysis of the diazo compound **7**. The ESR signal decayed immediately when the photolysis was stopped. The kinetics were determined analogously to that of the diphenylcarbene work.



7 6

The decay kinetics of **6** in propanols, 2-MTHF, or 2-MTHF-benzyl alcohol were best described by a log $I$ vs. $t^{-1/2}$ dependence. The kinetics of **6** were much faster than those of **2** in each glass. The decay of **6** occurred at 10–24 K lower temperature than those of diphenylcarbene (see Table V), although the concentrations of diazo precursors **2** and **7** were comparable. The higher reactivity of **6** relative to diphenylcarbene can arise from at least two effects. Either fluorenyidene is intrinsically more reactive (lower barrier heights) than diphenylcarbene or diazofluorenylidene solutions have more reactive sites than **1** (shorter tunneling barrier widths). The former interpretation seems more likely due to the similar size of the two diazo compounds. The Arrhenius parameters of fluorenylidene decay are again extremely small and indicate hydrogen atom tunneling reactions. The reported log $A$ values are actually negative. However, as with diphenylcarbene, there is tremendous imprecision in these measurements.

Table VI. Percent Decay of Triplet 1 in Various Crystals at 77 K After 1 h

| | | | |
|---|---|---|---|
| 1,3-cyclohexadiene | 84 | cyclohexane | 10 |
| cyclohexene | 78 | toluene-$d_8$ | 9 |
| toluene | 33 | styrene | 10 |
| 2-propanol | 17 | | |

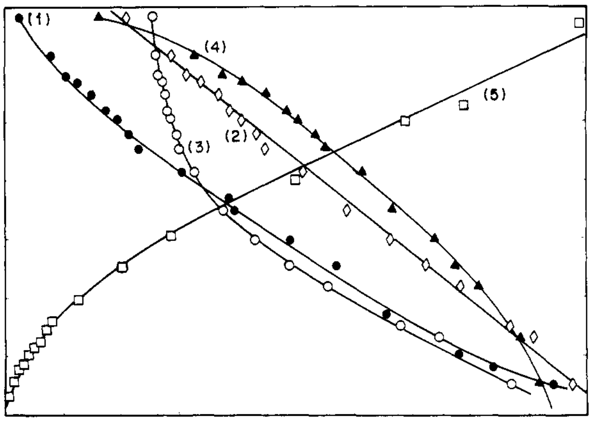
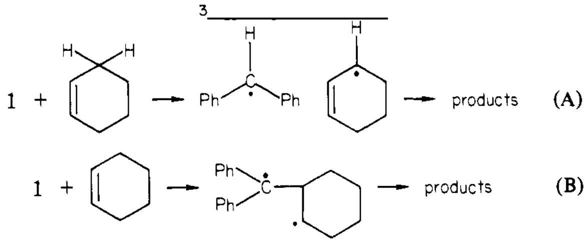


Figure 2. Plots of (1) log $I$ vs. $t^{1/2}$, (2) log $I$ vs. $t^{1/3}$, (3) log I vs. $t$, (4) log $I$ vs. log $t$, (5) $1/I$ vs. $t$ for diphenylcarbene triplet ESR $\Delta m \pm 2$ transition in 1:1 $C_6F_6$/toluene at −174 °C with $I_0 = 42$ and $I_\infty = 10$ at the end of 100 min.

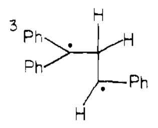
**Kinetics of Arylcarbenes with Organic Crystals.** The reactions of **2** and **6** were studied next in organic crystals. The rate of decay of diphenylcarbene in various crystals agrees with chemical intuition (see Table VI). **2** reacts sluggishly with cyclohexane, more rapidly with polycrystalline 2-propanol or toluene, and very rapidly with cyclohexene or 1,3-cyclohexadiene. The decay plots of log $I$ vs. $t^{1/2}$ in each crystal are not linear at long reaction times. The data do give a good fit to log $I$ vs. $t^{1/3}$ (see Figure 2). Site problems in polycrystals must be more severe than in glasses. The Arrhenius parameters (Table IX) are again characteristically low, indicative of tunneling processes. Triplet **1** can react with alkenes by at least two mechanisms, hydrogen atom abstraction–recombination (A) or by addition (B).



$^{3}$8

The triplet carbene decay mechanisms can be distinguished by substitution of styrene for cyclohexene. The rate of carbene reaction should be faster in styrene than in cyclohexene if the latter mechanism is operative. This follows simply from the relative stabilities of **8** and **9**.

The rate of reaction of **1** with styrene should be slower than the rate with cyclohexene in the former mechanism as styrene bears no abstractable allylic hydrogens. Experimentally, the ratio



9

$k$(cyclohexene)/$k$(styrene) = 144 (initial $k$ in $M^{-1}/s^{-1}$, 9% decay) at 77 K. The result is not completely definitive, as there may be a matrix site effect on the kinetics upon changing the host from cyclohexene to styrene. However, it does appear likely that hydrogen atom abstraction is faster than addition at 77 K, in agreement with the earlier findings of Moss.[5] This is not necessarily a consequence of the relative activation energies of abstraction vs. addition. It results from the suppression of all classical carbene reactions at 77 K in favor of hydrogen atom tunneling.

The observed pseudo-first-order decay of **1** ($k_{obsd}$) in 2-MTHF increases steadily as cyclohexene is added to the glass. If we were dealing with simple solution kinetics, then

$$k_{obsd} = k_1[\text{2-MTHF}] + k_2[\text{cyclohexene}]$$

From the limiting cases, [2-MTHF] = 0 or 10 M, $k_1$ and $k_2$ could be determined, and $k_{obsd}$ for the intermediate cases would be readily predicted. Naively applying this formula to the low temperature data predicts rate constants reasonably close to those observed (Table VII). The agreement is amazing when one considers the huge changes in phase that must be occurring in this solvent series. Fluorenylidene is more reactive in organic polycrystals than is diphenylcarbene (see Table VIII). To obtain comparable decay rates in toluene or 2-propanol, the fluorenylidene samples must be roughly 20 K cooler than the diphenylcarbene samples. This is entirely consistent with the aforementioned behavior of these two carbenes in glasses.

**Matrix Isotope Effects.** If the decay of arylcarbenes in low temperature matrices proceeds by hydrogen atom tunneling, the kinetics should be subject to unusual isotope effects. Williams found that the decay of methyl radicals in isotopically labeled hosts gave $k_H/k_D \sim 10^3$. The isotope effects observed with arylcarbenes are much more modest, and by themselves do not necessarily indicate tunneling. For fluorenylidene in toluene-$d_8$ (Merck, minimum isotopic purity >99%): matrix rate constants $k_H/k_D$ = 1.46 (77 K); initial rate constants (30% decay, $s^{-1}$) $k_H/k_D$ = 2.83. For diphenylcarbene in toluene-$d_8$: matrix rate constants ($s^{-1/3}$) $k_H/k_D$ = 6.92 (77 K); initial rate constants (10% decay, $s^{-1}$) $k_H/k_D$ = 23. Inspection of the respective Arrhenius parameters in these systems is much more revealing. For fluorenylidene–toluene matrix ($k$ in $M^{-1}\ s^{-1/3}$) parameters are $E_a(D) - E_a(H)$ = 344 cal/mol and $A_D/A_H$ = 6.4 (Table IX). If the initial decay rate constants are analyzed (30% decay, $k$ in $M^{-1}\ s^{-1}$), $E_a(D) - E_a(H)$ = 617 and $A(D)/A(H)$ = 19.5. The corresponding data for the diphenylcarbene–toluene matrix are: $E_a(D) - E_a(H)$ = 554 cal/mol, $A(D)/A(H)$ = 7.7, and initial (10% decay, $k$ in $M^{-1}\ s^{-1}$) $E_a(D) - E_a(H)$ = 1.2 kcal/mol, $A(D)/A(H)$ = 132 (see Figure 3 and Table X).

Caldin[21] has stated that "The difference in the observed activation energies is larger than it would be in the absence of tunnelling ... Any value of ($E_a$(D)-$E_a$(H)) larger than ... [1.1 kcal/mol] ... suggests that tunnelling may have to be taken into account ... Transition-state theory likewise predicts that A(D)/A(H) will not usually be greater than unity; the maximum value is 2 ... Any larger value of A(D)/A(H) is anomalous and suggests that tunnelling should be taken into account." The isotope effects observed between aryl carbenes and toluene-$d_8$ clearly support a tunneling mechanism.

Table VII. Effect of Cyclohexene Concentration on the Rates of Triplet Decay of Diphenylcarbene in 2-MTHF at 77 K

| cyclohexene concn[b] | $Ph_2C=N_2$, M × $10^3$ | $k$, $s^{-1/2}$ × $10^3$ | $k_{calcd}$, $s^{-1/2}$ × $10^3$ |
|---|---|---|---|
| 0 | 153 | 10.6 ± 0.4 | |
| 15 | 114 | 11.3 ± 0.5 | 12.4 |
| 30 | 188 | 13.4 ± 0.7 | 14.2 |
| 50 | 106 | 15.2 ± 0.8 | 16.6 |
| 100 | 88 | 22.6 ± 1.0[a] | |

[a] Plots better against $t^{1/3}$ initial rate. [b] Volume percent.

Table VIII. Triplet Decay Rates of Arylcarbenes in Crystalline Matrices (Plot: log $I$ vs. $t^{1/3}$)

| carbene | matrix system | diazo, M × $10^3$ | temp, K | $k$, $s^{-1/3}$ × $10^3$ |
|---|---|---|---|---|
| 1 | 2-propanol | 163 | 102 | 108.9 ± 2.2 |
| | | 163 | 106 | 118.0 ± 5.9 |
| 1 | toluene | 176 | 95 | 114.0 ± 5.9 |
| | | 176 | 99 | 147.7 ± 3.0 |
| | | 176 | 77 | 35.6 |
| 1 | toluene-$d_8$ | 168 | 77 | 5.15 |
| | | 105 | 103 | 85.10 |
| | | 105 | 109 | 148.50 |
| 1 | cyclohexane | 230 | 136 | 63.4 ± 3.17 |
| 1 | cyclohexadiene | 188 | 77 | 99.0 |
| 1 | cyclohexene ($C_6H_{10}$) | 88 | 77 | 82.2 ± 2.0 |
| 1 | styrene | 143 | 108 | 106.0 ± 4.0 |
| | | 143 | 118 | 146.5 |
| 6 | toluene | 115 | 77 | 73.26 |
| | | 115 | 88 | 132.70 |
| 6 | toluene-$d_8$ | 101 | 77 | 29.7 |
| | | 101 | 88 | 67.3 |
| 6 | 2-propanol | 16 | 77 | 69.3 ± 6.0 |
| | | 16 | 88 | 113 ± 6.0 |
| 1 | $C_6F_6$-$C_6H_{10}$ (1:1) | 33 | 87 | 71.3 ± 4.0 |
| 1 | $C_6F_6$-toluene (1:1) | 33 | 99 | 95 ± 6.0 |
| 1 | $C_6F_6$-propanol (1:1) | 33 | 99 | 95 ± 8.0 |

Table IX. Arrhenius Parameters of Triplet Decay of Arylcarbenes in Crystalline Matrices

| carbene | matrix | log $A$ | $E_a$, cal/mol |
|---|---|---|---|
| 1 | 2-propanol | −1.1 ± 0.01 | 503 ± 10 |
| 1 | toluene | 0.85 ± 0.03 | 1219 ± 20 |
| 1 | toluene-$d_8$ | 1.14 ± 0.022 | 1773 |
| 6 | 2-propanol | 1.108 | 934 |
| 6 | toluene | −0.873 | 388 |
| 6 | toluene-$d_8$ | −0.069 | 732 |

Table X. Initial Pseudo-First-Order Rate Constants and Arrhenius Parameters

| carbene | matrix | % decay | $k$, $s^{-1}$ × $10^3$ | temp, K | log $A$ | $E_a$, cal/mol |
|---|---|---|---|---|---|---|
| 1 | toluene | 10 | 3.21 | 77 | 1.24 | 1671 |
| | | | 30.3 | 95 | | |
| | | | 33.3 | 99 | | |
| 1 | toluene-$d_8$ | 10 | 0.14 | 77 | 3.36 | 2878 |
| | | | 13.9 | 103 | | |
| | | | 55.6 | 109 | | |
| 1 | cyclohexene | 9 | 41.7 | 77 | | |
| 1 | styrene | 9 | 0.29 | 77 | | |
| 6 | toluene | 30 | 5.1 | 77 | 0.85 | 1471 |
| | | | 16.5 | 88 | | |
| 6 | toluene-$d_8$ | 30 | 1.8 | 77 | 2.14 | 2088 |
| | | | 9.8 | 88 | | |

**Implication of Kinetic Data to Predict Studies.** The data indicate that some portion of diazo precursor (**2** or **7**) is photolytically converted to a long-lived triplet carbene at low temperature. The kinetics of the observable triplet are subject to matrix effects. The low Arrhenius parameters for the observable triplet decay indicate that the hydrogen atom abstraction–recombination products observed by Moss and Tomioka are formed by a tunneling mechanism.

The percent conversion of diazo compound to ESR active triplet was not determined. In general, this type of spin count is very

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(21) Caldin, E. F. *Chem. Rev.* **1969**, *69*, 135–156.

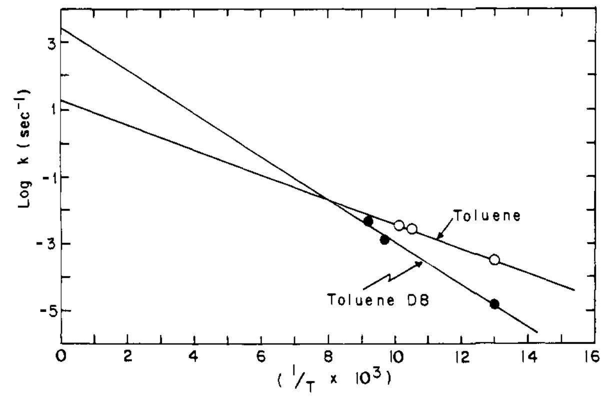

**Figure 3.** Arrhenius plots for diphenylcarbene-toluene (toluene-$d_8$) based on initial decay rate constants.

imprecise, particularly for metastable species. It is certainly possible that some portion of the original sample of the diazo compound will eventually form products without involving the observed triplet. For example, some percentages of products may arise from very fast singlet or triplet decay processes that were not observed. The photolysis of **2** or **7** and resultant extrusion of nitrogen may cause local heating in the sample. The nascent carbene is generated in a softened matrix and may react quickly before thermal equilibrium is reestablished with the bath. Alternatively, bimolecular reactions of photoexcited diazo compound with the host are possible and could lead to products.[22]

The ESR active triplet carbenes are sufficiently long-lived at 77 K to undergo secondary photolysis, particularly after most of the diazo precursor has been decomposed. Secondary photolysis of matrix isolated triplets has been reported. Photochemical decomposition of **1** has been observed by Trozzolo,[23] and Turro has observed secondary photolysis of biradical **5** even at very short irradiation times.[24] Irradiation of the triplet carbene can lead to products via the population of a highly reactive electronically excited state of the carbene or by local heating and softening of the matrix. All decay mechanisms that bypass the observed triplet carbene are invisible to this ESR study.

Prolonged photolysis of matrix isolated diazo compound, and the subsequent carbene reactions, alter the matrix (see Table IV). This suggests that the product mixture obtained at the early stages of the preparative matrix photolysis may be subtly different from the carbenes generated at long photolysis time.

## Conclusions

The kinetics of arylcarbene bimolecular reactions in glasses and crystals can be measured by ESR. The kinetics are sensitive to the chemical nature of the matrix, the viscosity of the matrix, the concentration of diazo compound, and the history of the sample with respect to photolysis. One effect of the matrix is to cause nonexponential signal decay. The data can be fitted to either a $t^{1/2}$ or $t^{1/3}$ vs. log $I$ dependence. The Arrhenius parameters and toluene isotope indicate that hydrogen atom tunneling reactions are the major decay pathways in the low temperature matrices. This explains the dominance of hydrogen abstraction-recombination products observed by other workers at low temperature.

## Experimental Section

Diphenyldiazomethane and 9-diazofluorene were prepared by oxidizing the corresponding hydrazones with yellow HgO in the presence of anhydrous $Na_2SO_4$ and a small amount of saturated ethanolic KOH solution, in ether.[5,6] They are recrystallized from cold pentane to remove ketazine. The purity was checked by IR, NMR, and TLC.

Most of the solvents are of spectrograde quality and are purified by distillation and stored over appropriate drying agents. Alkane solvents were mixed with concentrated sulfuric acid (1:1 ratio) and stirred for 24 h. The separated hydrocarbon is distilled and the constant boiling fraction collected and stored in air-tight bottles.

Solutions of low concentrations of diazo compounds were prepared by weight and higher concentrations were prepared by volume. As far as possible the ESR tubes used are identical. This was checked in the following way: a low concentration of diphenyldiazomethane in 2:3 1-propanol-2-propanol was prepared and placed in several tubes which are vacuum sealed, using three freeze-thaw cycles. At −175 °C the sample is irradiated for a fixed time in the ESR cavity using a 150-W xenon lamp. The intensity of the triplet signal is recorded at constant instrument settings. Those tubes which give equal initial signal intensities are considered identical. The ESR instrument used in this work is the Varian E-112.

Temperature control is carried out by employing a variable temperature control accessory attached with the instrument. All temperatures above −196 °C were obtained by passing regulated amounts of $N_2$ gas through the cavity. The $N_2$ gas is precooled by passing through liquid nitrogen. The exact temperature of the probe is measured by inserting an Omega digital thermometer into the cavity before and after each kinetic run. The data are analyzed only when there has been no temperature drift. The thermometer has an accuracy of ±0.5 °C. The temperature can be kept constant for several hours. The irradiation was passed through Schoeffel infrared filters to reduce sample heating. For kinetics at liquid nitrogen temperature, the sample tube is placed in a Dewar flask containing liquid nitrogen.

Pseudo-first-order kinetics are followed by observing the decay of signal intensity of the transition of the triplet at ~1150-G field strength. The transition can be conveniently recorded and the time at which the pen crosses the peak maximum noted. The base line is drawn and the height of the peak maximum from the base line is used as a measure of the intensity of the triplet radicals at that time. In all the kinetic runs the signal is recorded up to 70–85% of decay, from which the rate constants are calculated by plotting the log [intensity] vs. $t^{1/2}$ or $t^{1/3}$, whichever may be the case. The rate constants reported are obtained by graphical methods excepting the values in Table III, which are obtained with a calculator using the least-squares fit program. The correlation coefficients obtained are always 0.999–1.0. The reproducibility in rate constants was found to be ±5.0% in all the cases.

**Acknowledgment.** We gratefully acknowledge support of this work by the National Science Foundation (Grant No. CHE-7900896).

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[22] Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072–3075.

[23] Gibbons, W. A.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 172–173.

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