# Atom-Transfer Reactions of Aromatic Carbenes

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Many reactions in organic chemistry, particularly those initiated photochemically, involve short-lived, highly reactive species that cannot be isolated and characterized by ordinary methods.[1] It is a major goal of physical organic chemistry to characterize transient intermediates with the same degree of sophistication as is possible in the study of isolable molecules. Matrix isolation is a frequently employed tool in this regard.[2] In an ideal experiment, photolysis of a precursor (e.g., diazomethane (1)) generates a new species surrounded

$$CH_2N_2 \xrightarrow[h\nu]{\text{argon, 10 K}} CH_2 + N_2$$
$$1 \qquad\qquad\qquad 2$$
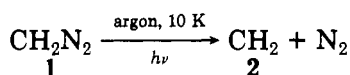
by a rigid inert host (e.g., argon). The photogenerated species (e.g., methylene (2)) may have a lifetime of minutes, hours, or even days in the matrix even though its lifetime in mobile solution may be in the nanosecond time regime.

The long matrix lifetime allows convenient spectroscopic characterization. In this regard electron paramagnetic resonance (EPR) spectroscopy has proven to be a powerful tool in the study of triplet carbenes.[3]

The majority of studies of the organic chemistry of carbenes have been performed in the solution phase, and one can properly question the relevance of the low-temperature spectroscopy to the reactivity patterns observed at temperatures that may be hundreds of degrees higher.[4] In a seminal experiment Moss and Dolling demonstrated that carbenes do undergo chemical reactions at the low temperatures used under conditions that are typical of matrix EPR, and that these reactions are *strikingly different* from those observed in solution.[5]

The early results were representative of a number of later studies reported by Moss and co-workers,[6] by Tomioka,[7] and by ourselves.[8] Low-temperature solid-state conditions dramatically enhance the yields of formal C–H insertion adducts between the photogenerated carbene and the matrix host. The key question for us at the outset of our studies was the mechanism of the matrix effect on the product distributions. Our investigations have led to an appreciation of the energetics of atom-abstraction reactions of carbenes, the role of quantum mechanical tunneling in these processes, the relative magnitudes of singlet–triplet energy splittings in carbenes, singlet–triplet surface crossings on reaction pathways, and the generation and EPR spectroscopy of certain triplet biradicals.

Kinetics of Decay of Triplet Carbenes in Glasses and Polycrystals As Measured by EPR

In 1980 Lin and Gaspar[9] and Senthilnathan and Platz[10] reported the use of EPR to monitor the decay of simple triplet carbenes such as diphenylcarbene (DPC), fluorenylidene (Fl), 1-naphthylcarbene (NC), and dibenzocycloheptadienylidene (DBC). The EPR
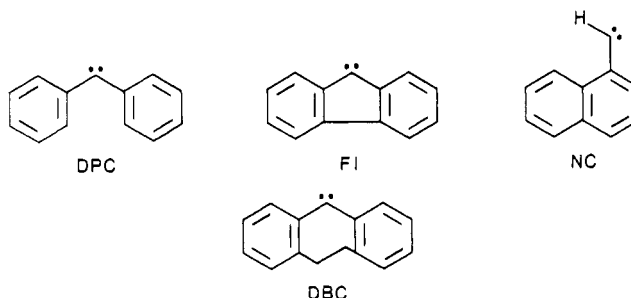
spectra of the carbenes were produced by brief photolysis of the corresponding diazo compounds, and the rate of signal disappearance was measured immediately after photolysis was discontinued. We attributed the decay of the triplet carbenes in hydrocarbon hosts to H-atom abstraction from the matrix, based on the following evidence: (1) the aforementioned product studies, (2) a kinetic isotope effect (KIE) upon perdeuteriation of the matrix, (3) the absence of any carbene decay in perfluorinated matrices, and (4) the fact that the rate of carbene decay roughly followed the

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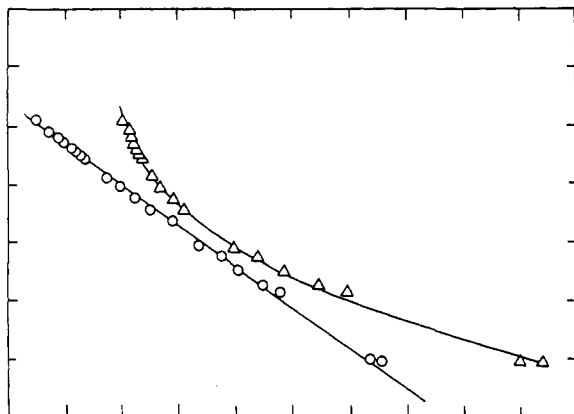
Figure 1. Plots of ln (I/I_0) versus time ($\triangle$) and (time)$^{1/2}$ (O) obtained from the decay of DPC in a propanolic glass at 98 K taken to 80% signal disappearance.

Figure 2. Initial rate data plotted as ln (I/I_0) versus time for DPC in diethyl ether at 93 K.

expected order of H-atom-donating ability of the matrix.

The rate of carbene decay is affected by a number of factors (diazo concentration, the extent of photolysis, sampling history, etc.). Nevertheless, when these factors are kept constant, reproducible decay curves can be obtained. Unfortunately, the decay curves of the triplet carbenes are not exponential as expected from the product studies and the proposed decay mechanism; plots of ln (I/I_0) versus t (where I = signal intensity and t = time) were quite curved (Figure 1). Curiously, plots of ln (I/I_0) versus $t^{1/2}$ were frequently linear.[10] This phenomenon has been observed previously in the dynamic behavior of radicals and excited states in polycrystalline solids and attributed to a multiple-site problem.[11]

The prototypical H-atom-abstraction reaction of triplet methylene and methane has been studied by Schaefer and Bauschlicher at the ab initio level of theory.[12] The migrating methane hydrogen is in the plane of methylene and along the line of bisection of the HCH bond angle.

$$\begin{array}{c} H \\ \diagup \\ \diagdown \\ H \end{array} \!\!\!\!\!\!\text{------}\, H\text{---}CH_3 \;\longrightarrow\; 2CH_3{}^\bullet$$
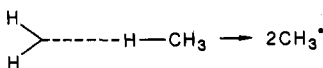
The calculated activation energy is 7 kcal/mol. Less symmetric in-plane H-atom migration and out-of-plane H-atom transfer must of course surmount higher potential energy barriers to complete the reaction.

Rapid cooling of a solution of a diazo compound such as 9-diazofluorene in toluene to 77 K, followed by subsequent photolysis generates Fl in a multitude of different local environments with respect to ease of reaction with the matrix. There are a few sites in which Fl and toluene can realize the ideal transition-state structure, and carbenes in this site will react the most rapidly. Obviously, sites with poorer configurations will react more slowly. Because the sites do not equilibrate, depletion of a site is irreversible. In this manner the observed rate of decay of a carbene continuously decreases during an experiment, and consequently the carbene decay is more complex than can be described
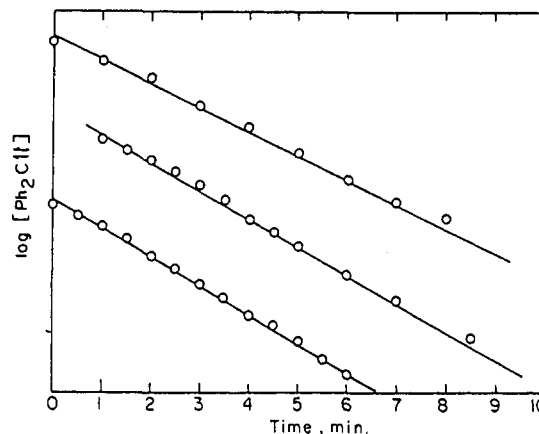
Table I
Pseudo-First-Order Arrhenius Parameters for the Initial Decay of DPC in Various Matrices

matrix	E_a, kcal/mol	log A, s^{-1}	A_H/A_D
toluene	2.1	2.4	0.0625
toluene-d_8	3.1	3.6	
diethyl ether	2.9	5.4	
diethyl-d_{10} ether	4.0	7.4	0.01
benzene	4.3	4.1	
benzene-d_6	5.3	5.4	0.005
methylcyclohexane	2.8	2.3	
methylcyclohexane-d_{14}	3.6	3.6	0.005
cyclohexene	3.2	2.0	
cyclohexene-d_{10}	4.5	2.7	0.005

by a simple exponential. Perhaps it is only fortuitous that radicals and carbenes under certain conditions appear to follow a $t^{1/2}$ rate law. Knowing this "answer", it is possible to "work backward" and derive a distribution of sites that will give this apparent rate law.[13,14]

The nonexponential decays of Fl, DPC, 1-NC, and other carbenes complicate the analysis. In order to make any progress we made a crucial assumption that the first 20% of the carbene signal decay corresponded to the decay of the carbene in a single unique site.[15] Plots of ln (I/I_0) versus time in this regime were linear, and the slopes were equated to an absolute rate constant for a specific site (Figure 2). The temperature dependencies of these "rate constants" were determined and gave the unusual data of Table I. Both the Arrhenius activation energies and preexponential factors were much smaller than expected for a simple H-atom transfer.[15,16] The temperature dependence of the isotope effect was also unusual. The ratios of A_H/A_D were smaller than the limits acceptable within the framework of Bigeleison's transition-state calculations.[17] On this basis, and perhaps with more courage than wisdom, we proposed that quantum mechanical tunneling (QMT) was the mechanism of the matrix H-atom transfer.

We were supported in this view by the complete lack of reactivity of triplet diarylcarbenes in chlorocarbon

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(13) (a) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 175. (b) Doba, T.; Ingold, K. U.; Siebrand, W. *Chem. Phys. Lett.* **1983**, *103*, 339. (c) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *J. Phys. Chem.* **1984**, *88*, 3163. (d) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *Chem. Phys. Lett.* **1985**, *115*, 51.

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Table II
**Selected Experimental and Best Fit Pseudo-First-Order
Initial Rate Constants for Reaction of DPC in a Toluene
Matrix**[a]

temp, K	k_{expt}, s^{-1}	k_{calcd}, s^{-1}
77	0.00063	0.00073
95	0.0046	0.0036
99	0.0067	0.0060
103	0.0095	0.011
106	0.017	0.018

[a] Toluene: ΔE_a(classical) = 6.9 kcal/mol, barrier width parameter = 1.25 Å; toluene-d_8: ΔE_a(classical) = 6.8 kcal/mol, barrier width parameter = 0.766 Å; diethyl ether: ΔE_a(classical) = 6.5 kcal/mol, barrier width parameter = 1.37 Å; diethyl-d_{10} ether: ΔE_a(classical) = 5.4 kcal/mol, barrier width parameter = 0.940 Å.

matrices at 77 K. Product studies and CIDNP spectroscopy had demonstrated that both singlet and triplet carbenes can abstract chlorine atoms from chlorocarbons,[18] yet DPC and Fl are completely stable in carbon tetrachloride matrices at 77–100 K.[19,20] QMT provides a simple explanation: the small light H atom can tunnel but the more massive Cl atom cannot.

QMT also explains the dramatic switch in carbene chemistry observed upon changing from the liquid to the solid phase.[5–8] In the solid state, reactions requiring large nuclear displacements will be retarded by the rigid matrix environment. H-atom transfer from the matrix to the carbene to form a radical pair is a least-motion process. This mechanism dominates the carbene decay not because it is particularly fast but because the competing processes have become exceedingly slow in a rigid solid. Perhaps the small yield of cyclopropanes observed in olefinic matrices originates from the few sites in the polycrystal where nascent carbenes are generated with an ideal orientation for cycloaddition relative to the carbon–carbon double bond of the host alkene.[21]

Because the rate of a QMT process does not go to zero, even at absolute zero, QMT would seem to be a natural explanation for how a reaction (H-atom transfer) could proceed in minutes at 77 K despite an anticipated activation energy of several kcal/mol.[22] With the considerable help of my colleague Bill McCurdy, the kinetics of reaction of DPC with various matrices were fit to a one-dimensional tunneling model developed by LeRoy.[15,23] The tunneling rate constant is a function of the barrier height and width, the reaction exothermicity, the mass of the tunneling atom, the zero-point energy of the CH bond which is the H-atom donor, and the temperature. Temperature affects the rate by affecting the Boltzmann distribution over the vibrational levels of the reactant. LeRoy has also introduced a coupling of the vibrational levels to the breathing modes of the matrix, thereby broadening the vibrational level in a temperature-dependent way. All of the variables for the matrix reactions of DPC were known except the

barrier height and width. These parameters were systematically varied by using a nonlinear least-squares routine to achieve a best fit of theory to the experimental data.[15]

The agreement between calculated and observed rate constants was quite good (Table II), but this was not surprising considering the narrow temperature range. However, the magnitudes of the calculated barrier heights (Table II) compared well with those observed for H-atom-transfer reactions of organic radicals and are in the range predicted by the ab initio calculations of Schaefer.[12] This encouraged us to think that our initial, crucial "single-site" assumption was not too extreme and that perhaps over a 20 K temperature interval it was possible that the same site could be monitored in the initial 20% of the carbene decay.

Unfortunately, a skeptical view of the QMT interpretation was depressingly strong in 1982. Typical KIE's measured at a single temperature were less than a factor of 10 even though our own calculations[15] placed the values closer to 10^4! We apologetically claimed that we monitored the decay of different sites in a matrix and its deuteriated modification. The initial decay rates measured in toluene, for example, would correspond to a rather slowly reacting site, most of the reactive sites in toluene being too fast for us to measure. In toluene-d_8, however, sites that were too fast to measure in toluene were dramatically slowed in rate by the KIE and could now be resolved. Thus KIE's were low because we had compared "unreactive" toluene sites to "highly reactive" toluene-d_8 sites. This was in line with our own calculations, which showed barrier widths of 1.25 and 0.760 Å in toluene and toluene-d_8 matrices, respectively.

Chemical evidence suggested that the true "KIE's" were actually quite large but were obscured by site problems. Photolytic generation of DPC or Fl in a matrix of 1:1 toluene:toluene-d_8 gave the resulting formal CH insertion adducts 3 and 4. The chemically determined isotope effect was again small. However, generation of DPC or Fl in a matrix of toluene-α-d_1 favored H over D transfer by greater than 100:1, the limit of NMR sensitivity.[24]

3   4   5
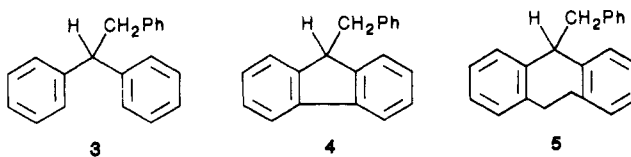
At this point we reasoned that in the toluene:toluene-d_8 matrix there was not an unimpeded competition for H versus D donors. The carbenes reacted only with the atom donor they were generated next to. In toluene-α-d_1 the KIE is much more realistic because the H and D are on the same carbon atom and presumably more equally accessible to the carbene, assuming, of course, free methyl group rotation at 77 K. Thus in 1982 the QMT hypothesis was tenuous at best. The multiple-site problem invalidates the use of the Arrhenius data of Table I to support QMT. Continued work over the next 5 years demonstrated that the premise was indeed correct and yielded a keener insight into the mechanisms of atom-transfer reactions of

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(19) Wright, B. B.; Kanakarajan, K.; Platz, M. S. *J. Phys. Chem.* **1985**, *89*, 3574.
(20) This is probably not due to aggregate formation in CCl$_4$, as the addition of 20% CCl$_4$ to 2-methyltetrahydrofuran (MTHF) results in a clear, apparently homogeneous glass but does not substantially increase the decay rate of the carbene relative to pure MTHF.[20] Maloney, V. M. Ph.D. Thesis, The Ohio State University, 1987.
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(22) (a) Bell, R. P. *The Tunnel Effect in Chemistry.* (b) Caldin, E. F. *Chem. Rev.* **1969**, *69*, 135.
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(24) Savino, T. G.; Soundararajan, N.; Platz, M. S. *J. Phys. Chem.* **1986**, *90*, 919.

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

glass	high temp			low temp		
	range, K	log (A/s^{-1})	E_a, kcal/mol	range, K	log (A/s^{-1})	E_a, kcal/mol
MCH/T[a]	122–103	14.0	5.3	103–90	6.0	1.2
E[b]	143–123	16.4	7.0	123–95	5.0	1.7
PG[c]	222–189	12.9	7.9	189–165	5.1	1.3
2MTHF[d]	109–96	18.1	6.0	95–87	10.7	2.9
CCl$_3$F/CF$_2$BrCF$_2$Br	136–116	8.6	1.8	106–87	9.1	2.1

[a] Methylcyclohexane/toluene. [b] Ethanol [c] 1,2-Propanediol. [d] 2-Methyltetrahydrofuran.

carbenes in matrices and in solution.

EPR Analysis of the Radical Pair Products

Reaction of a triplet carbene (e.g., DBC) with a matrix (MH) by atom transfer forms a triplet radical pair (RP) which can also be detected by EPR.[25] Brief
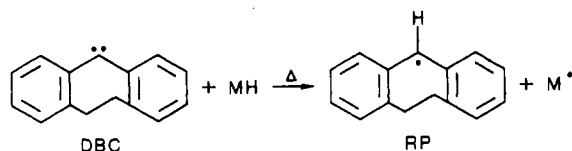
photolytic generation of DBC or Fl immediately produces RP-like spectra. However, the intensities of the DBC–MH-derived radical pair spectra continued to increase in the dark, and as far as we could determine the RP grew in at the same rate at which the carbene decayed. Photolytic generation of DPC or Fl in a deuteriated matrix again immediately produced a RP-like spectrum, but there was absolutely no continued spectral growth once photolysis was stopped. These observations persuaded us that the RP EPR spectra were carbene derived but led us to another question. Why isn't the dark decay of DBC or Fl in a deuteriated matrix accompanied by an increase in the RP product? The answer is simple: the KIE in the deuteriated matrix is so large that the carbene finds something else to do![26] This was demonstrated by product studies; photolysis of diphenyldiazomethane in toluene at 77 K gives a nearly quantitative yield of 3. Photolysis in toluene-d_8 gave less than a 35% yield of the corresponding product. Similar results were obtained with DBC. The small amount of adduct formed in toluene-d_8 at 77 K and the RP's produced in protic and deuteriated matrices during the photolysis of diazo compounds can now be recognized as arising from secondary photochemical reactions of the matrix-isolated carbenes.
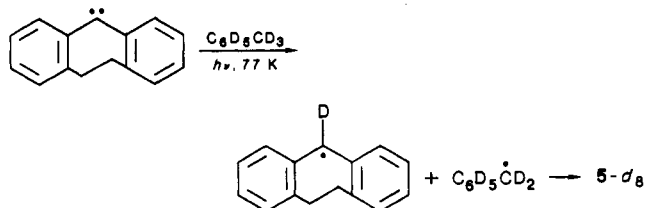
This was proven by studying the signal intensity of the RP product as a function of light intensity and wavelength.[25] It was possible to photolyze 9-diazofluorene at 77 K with long-wavelength light to produce

(25) Barcus, R. L.; Wright, B. B.; Leyva, E.; Platz, M. S. *J. Phys. Chem.* 1987, *91*, 6677.
(26) The principal decay route of triplet carbenes in non-hydrogen-atom-donating glasses is reaction with diazo precursor to give azines and dimerization.
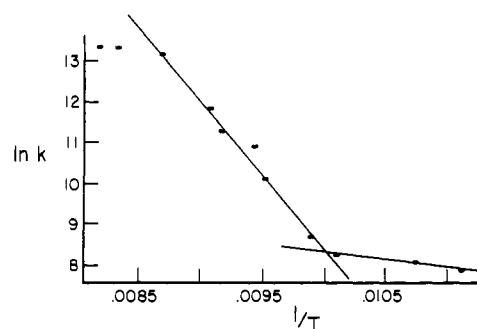
Figure 3. Arrhenius plot of the pseudo-first-order decay of Fl in MCH/T.

the Fl EPR spectrum, free of a RP spectrum. Short-wavelength photolysis of matrix-isolated Fl then produced the RP spectra. Our previously determined low KIE's were now properly recognized as red herrings. The reported KIE's actually were the ratios of the H-atom-transfer rates to the rates of side reactions in the deuteriated matrix.[26]

Laser Flash Photolysis Studies of Carbenes in Low-Temperature Glasses

The poor time resolution of conventional EPR limited our studies to the fastest resolvable site in a given matrix. There was no guarantee that we were monitoring the same site as the temperature was varied. There was also concern that our fastest resolvable sites were atypically slow and were the most perturbed by the matrix. Thus we turned our attention to a technique with greater time resolution, laser flash photolysis (LFP) of diazo precursors in optically clear, cold glasses.

Laser flash photolysis of DAF was studied in a number of glasses and the pseudo-first-order decay of Fl recorded.[27] In contrast to our EPR studies, exponential decays were observed. The Arrhenius treatment of the data obtained in methylcyclohexane/toluene (MCH/T, glass 1) is shown in Figure 3. The plot is typical of all of the hydrogen-containing glasses studied. Two regions are observed, a steep region at high temperatures with normal Arrhenius parameters (Table III) and a flat, temperature-insensitive region with very low activation parameters. These plots are completely consistent with a H-atom-transfer reaction in which the reaction mechanism changes from a completely classical process in a soft warm glass to a completely QMT process in a cold hard glass.[22]

Upon extrapolation of the high-temperature data to the low-temperature regime, one finds that the observed rate is hundreds of times faster than predicted. In methylcyclohexane/toluene, the viscosity decreases by 9 orders of magnitude between 122 and 90 K (Table

(27) Ruzicka, J. A. M.Sc. Thesis, The Ohio State University, 1985.

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

temp, K	k, s^{-1}	viscosity, P	k_{diff},^{a} M^{-1} s^{-1}
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 $^\circ$Fl with MCH/T can be converted to a pseudo-first-order rate constant (and compared directly with k, s^{-1}) by multiplication by 10 M, the approximate molarity of the glass.
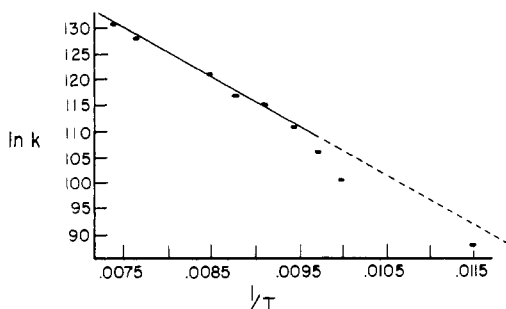

Figure 4. Arrhenius plot of the pseudo-first-order decay of Fl in CFCl$_3$/CF$_2$BrCF$_2$Br.

IV). It is a simple matter to imagine that the rate of a given bimolecular reaction will decrease as the diffusion rate is drastically reduced, but why should more limited molecular motion in a glass dramatically increase the reaction rate? QMT provides a convenient explanation. When the rate of classical H-atom abstraction has been reduced due to increased viscosity, the rate of QMT becomes isokinetic and then faster than the classical process.

Converting the measured pseudo-first-order rate constants to bimolecular rate constants yields values that are considerably faster than the calculated diffusion-controlled rate constants (Table IV). One must view the matrix reaction as "unimolecular" because the reacting partners are held rigidly to form a single kinetic unit. It is also interesting to compare the first-order rate constants measured by EPR and by laser flash photolysis; the EPR numbers are much smaller, implying that this technique missed most of the reaction at 77 K (at least for Fl) and monitors only the least reactive sites, the very sites in which the reaction has been most distorted by the matrix.

If there is no change in mechanism over the temperature interval depicted in Figure 3, then we would expect an Arrhenius plot that is curved downward, opposite to what we have observed. The Arrhenius plots in all H-atom-donating glasses are curved upward. We are aware of only one non-hydrogen-containing glass that dissolves DAF.[28] The Arrhenius plot in this glass, where QMT is impossible, is linear or perhaps slightly curved downward (Figure 4). The chemistry responsible for carbene decay in this glass is incompletely understood.

(28) Grimison, A.; Simpson, G. A. *J. Phys. Chem.* **1968**, *72*, 1776.
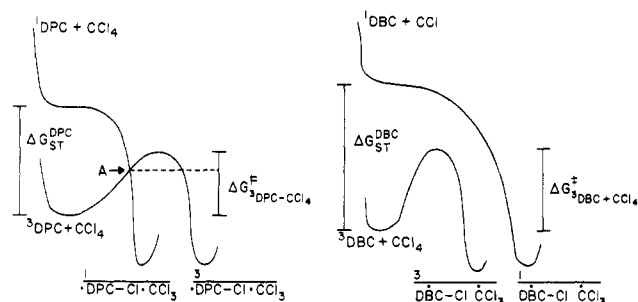
**Figure 5.**

Table V
Arrhenius Parameters for the Reaction of Triplet Carbenes with Various Quenchers in Chlorobenzene-Substrate Mixtures[29]

carbene	quencher	E_a,^{a} kcal/mol	log $(A/(M^{-1} s^{-1}))^a$	k^{300K}, M^{-1} s^{-1}
DPC	diethyl ether	3.9 ± 0.6	7.8 ± 0.5	7.1×10^4
DPC	toluene	3.6 ± 1.7	7.2 ± 1.3	3.8×10^4
DPC	CCl$_4$	1.5 ± 0.3	7.4 ± 0.2	2.0×10^6
DPC^b	methanol	2.5 ± 0.4	9.3 ± 0.3	3.1×10^7
DPC^c	methanol	1.2 ± 0.4	8.2 ± 0.3	2.0×10^7
DBC	diethyl ether	3.7 ± 0.9	7.8 ± 0.7	1.3×10^5
DBC	CCl$_4$	6.7 ± 1.5	9.4 ± 1.1	3.5×10^4
DBC^d	methanol	5.0 ± 1.0	9.1 ± 0.8	2.5×10^6

^{a} All errors reported as $\pm 2\sigma$. ^{b} In chlorobenzene, from ref 27. ^{c} In benzene. ^{d} In toluene.

Do the biphasic Arrhenius plots indicate a change in mechanism from triplet to singlet matrix chemistry? We think this is unlikely in hydrocarbon glasses because Moss has studied the chemistry of DPC and Fl in a matrix of labeled isobutylene.[6] The scrambling of the label in the product was consistent with triplet rather than singlet chemistry of the carbene.
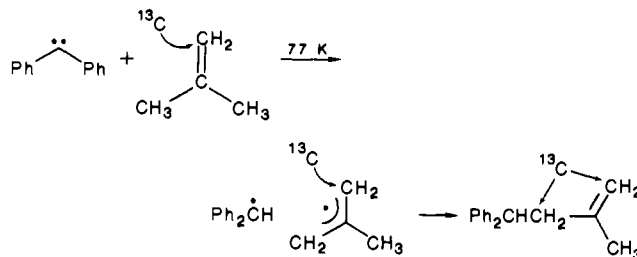
Laser flash photolysis of DAF in MCH-d_{14}/T-d_8 was attempted in the hopes of obtaining a realistic single-site KIE. Unfortunately, the kinetics were severely nonexponential and product studies indicated that reaction with C–D bonds was of only minor importance in this matrix.

Solution-Phase Flash Photolysis

The low-temperature EPR kinetic data for DPC could be fit to a one-dimensional Eckart barrier (Table II)[15] to ultimately predict the activation energy of a purely classical H-atom transfer. The measured solution-phase activation energies for DPC are listed in Table V and are 2.3–3.3 kcal/mol lower than the predicted values for diethyl ether and toluene, respectively.[29] Depending on one's point of view, this can be taken either as reasonably close agreement to the Eckart barrier calculations or a serious disagreement.

(29) Barcus, R. L.; Platz, M. S.; Scaiano, J. C. *J. Phys. Chem.* **1987**, *91*, 695.

However, the measured activation energies and preexponential factors are exceedingly small (Table V) for a typical H-atom-transfer reaction (E_a = 14.3 kcal/mol and A = $10^{8.8}$ M^{-1} s^{-1} for the reaction of methyl radical with methane).[30]

It occurred to us that there may be a small contribution of QMT to a largely classical H-atom-transfer process in solution. There is a qualitative difference between QMT at high and at low temperature. In low-temperature solids the reaction is pure QMT from the lowest vibrational levels of the reactants. In solution at elevated temperatures the QMT occurs to a minor extent in competition with classical H-atom transfer and occurs from vibrational levels near the top of the barrier.

To test for solution-phase QMT we chemically determined the KIE for several carbenes with toluene over 100 K.[31] For DPC the data are barely within the limits of transition-state theory, but more sterically hindered carbenes had unmistakable QMT contributions (E_a(D) − E_a(H) > 1.2 kcal/mol; A_H/A_D < 0.5). This is another example of an increase in the importance of QMT because the rate of the competing classical process has become retarded. This would move the experimentally determined classical barriers even closer to those calculated from the asymmetric Eckart functions.

Singlet–Triplet Surface Crossings

The activation parameters for the reaction of triplet DPC and DBC with diethyl ether, carbon tetrachloride, and methanol are also given in Table V.[29] The data for the H-atom-transfer reaction of the two carbenes with ether are similar, but DBC and DPC react in a markedly different manner with CCl$_4$ and methanol. The H-atom-transfer reaction with ether stays completely on the triplet spin surface for both carbenes.

$$Ph_2C\uparrow\uparrow + RH \rightarrow Ph_2CH\uparrow + R\uparrow$$
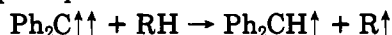
However, in the methanol reaction the reactants have triplet spin multiplicity and the reaction product has singlet multiplicity; thus at some point there is a spin inversion along the reaction coordinate

$$Ph_2C\uparrow\uparrow + CH_3OH \rightarrow Ph_2CHOCH_3$$

The similarity in activation parameters for each carbene with CCl$_4$ and methanol implies that the mechanism for carbene reaction with each of these reagents is the same. However, the difference in activation parameters between DPC and DBC indicates that their reaction mechanisms differ.[29] It was postulated that with DPC there is a surface crossing point at which the ^{3}DPC + CCl$_4$ surface crosses the ^{1}DPC + CCl$_4$ surface to form a singlet RP, hence the extraordinarily low E_a and A values. It was further postulated that in DBC the singlet–triplet energy gap is larger than the E_a for Cl-atom transfer; hence the reaction occurs completely on the triplet surface. The larger singlet–triplet gap in DBC can be attributed to its larger internal C–C–C angle relative to DPC,[32] destabilizing the singlet relative to the triplet state. The same explanations are applied to the methanol reaction, although RP intermediates are not involved. It must be pointed out though that this interpretation is controversial and

other viewpoints have been expressed.[33] Continued work in this area can be anticipated.

It is interesting to note that the solution-phase activation parameters of ^{3}DPC with CCl$_4$ predict a sizable absolute rate constant ($\sim10^2$ M^{-1} s^{-1}) at 77 K. The observed rate is almost 10^{10} slower than this, a dramatic illustration of the retardation of a classical atom-transfer rate by the matrix.[19]

Applications of H-Atom Transfer to the Spectroscopy of Biradicals

Finally we note that matrix H-atom transfer has been used to generate biradicals that can be studied by EPR. We have been able to prepare *m*-xylylene by photolysis of the appropriate 1,3-bis(diazomethyl)benzene to yield a bis(carbene) quintet at 23 K. Warming the matrix to 77 K leads to the disappearance of the quintet and the appearance of the EPR spectrum of *m*-xylylene.[34] The biradical is undoubtedly formed by double-H-atom abstraction from the matrix.

Photolysis of (8-methyl-1-naphthyl)diazomethane at 4 K does not produce a detectable carbene. The putative carbene immediately rearranges to form triplet 1,8-naphthoquinodimethane. We suspect that the intramolecular H-atom transfer is fast even at 4 K due to rapid QMT through a very thin barrier.

Conclusions

The goal of mechanistic analysis is to discover a simple concept that can provide a unifying framework which organizes a diverse body of experimental data. The success of the mechanistic hypothesis is measured by how many facts can be interpreted and how few assumptions are required to support the claim. By this criterion the H-atom transfer by QMT is the most successful interpretation. Ultimately our interpretation requires us to assume only that classical H-atom-transfer reactions occur more slowly in disordered solids than in solution. The interpretation explains the dramatic change in product distributions observed when carbenes are generated in solids rather than liquids. It explains why the carbene reactions occur in minutes at 77 K rather than hours, as expected on the basis of free radical model systems. It explains why triplet carbenes fail to react with chlorine-atom donors at 77 K, despite their often higher ratios of Cl-atom to H-atom transfer in solution. QMT explains our curved-upward Arrhenius plots obtained by laser flash studies in H-atom-donating glasses and is consistent with our curved-downward plot obtained in the perhalogenated glass. Our initial assumption of "single-site" kinetics used to analyze our EPR data is no longer crucial or even necessary for the QMT interpretation. Nevertheless, analysis of these initial rate data by QMT theories predicts solution-phase activation energies that are close to reality.

We confess that every piece of our supporting evidence can be rationalized without the aid of QMT. Yet each of these interpretations depends upon an ad hoc and untestable "matrix effect". Furthermore, different pieces of evidence require different "matrix effects";

(30) Gray, P. A.; Herod, A. A.; Jones, A. *Chem. Rev.* 1971, *71*, 257.
(31) Shaffer, M.; Platz, M. S. *J. Am. Chem. Soc.*, to be submitted.
(32) See: Shavitt, I. *Tetrahedron* 1985, *41*, 1531 and references therein.

(33) (a) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* 1985, *41*, 1525. (b) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferen, G.; Langan, J.; Cha, Y. *Tetrahedron* 1985, *41*, 1543.
(34) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* 1983, *105*, 628.
(35) Platz, M. S. *J. Am. Chem. Soc.* 1979, *101*, 3398.

thus there is at present no alternative, unifying mechanism that explains the matrix chemistry and kinetics of carbenes. Thus QMT remains the most economical and preferred interpretation at this time.