the end of a decay event. The two processes are represented by

$$T_s + T_m \rightarrow {}^1E^* + {}^1M_0 \qquad (3)$$

and

$$T_m + T_m \rightarrow {}^1M^* + {}^1M_0 \qquad (4)$$

followed by

$${}^1M^* + {}^1E_0 \rightarrow {}^1E^* + {}^1M_0 \qquad (5)$$

where ${}^1E_0$ represents a ground-state configuration involving two chromophore groups properly oriented to form a triplet excimer upon excitation. It has been assumed in the above discussion that process 3 is the major one for production of DF but if the population of T_s species drops to a sufficiently low value at the end of a decay event then processes 4 and 5 could occur at competititve rates. That the T_s population in P2VN does, in fact, decline relative to that of T_m may be seen from the spectra of Figure 5 where one notes the emergence of structured, nonexcimeric phosphorescence at long times after the excitation pulse. Clearly, no maximum in the DF-temperature profile would be expected under these conditions. A second possibility is that dual mechanisms for delayed fluorescence production are operating as was suggested by recent studies of Stolzenberg, Ries, and Bässler who propose an ion pair recombination process for solid films of PVCA.[19] In their experiments generally higher laser intensities were used and the temperature intervals were larger than those employed here.

Conclusions

The presence of a maximum in the intensity of DF as a function of temperature is found at 40 K from PVCA solid films. This is the second maximum of this type found for PVCA, the high-temperature one occurs at 200 K. The major mechanism for the production of DF in the temperature range from 10 to 150 K appears to be a triplet-triplet hetero annihilation involving a mobile triplet exciton and a trapped one. These results are in accord with previous temperature dependence studies in the range from 77 K to ambient. The disappearance of the low-temperature maximum at 40 K with DF intensity measurements at relatively long times after the excitation pulse may be understood in terms of a competition between hetero annihilation and homo annihilation modes of DF production with the latter winning out at longer delay times. There may also be a contribution to DF intensity at long times from geminate ion pair recombination.

For P2VN a similar study shows a maximum at 55 K in a graph of DF intensity versus temperature. the existence of these low-temperature maxima is thought to be due to the onset of detrapping of shallow triplet traps causing a reduction in the rate of hetero annihilative delayed fluorescence. The triplet trap depth in the case P2VN has been estimated to be 230 cm^{-1} from measurements of the rate of phosphorescence decay as a function of temperature and from the relative positions of monomeric and excimeric phosphorescence bands.

Time-resolved phosphorescence spectra of P2VN at 16 K include the emergence of a monomeric emission band which becomes more prominent as the delay time increases. At higher temperatures such as 77 K no monomeric phosphorescence is observed from P2VN and it is concluded that internal rotational modes have sufficient energy at the higher temperature so that neighboring chain units are able to probe many different conformations during the residence time of an excited triplet state. If one of these conformations corresponds to a stable excimeric state then the triplet will be trapped at that site. A necessary corollary to this conclusion is that the excimeric phosphorescence observed at 16 K must arise primarily from preformed excimer-forming sites.

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Registry No. P2VN, 28406-56-6; PVCA, 25067-59-8.

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Benzylbromocarbene: Absolute Rate Constant for 1,2-Hydrogen Migration and Ambiphilicity

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Laser flash photolysis studies of the reaction of benzylbromocarbene with pyridine enables the determination of the absolute rate constant for the 1,2-hydrogen migration in benzylbromocarbene. Thus, $k = 5.6 \times 10^7/\mathrm{s}^{-1}$ at 25 °C. Relative reactivities of benzylbromocarbene toward electron-poor and electron-rich alkenes indicate that the carbene is ambiphilic. The present results are consistent with a mechanism involving a carbene-alkene intermediate.

Introduction

The intramolecular 1,2-hydrogen migration to a carbene center that generates alkene has been a subject of considerable interest.[1] Extensive calculations[2-7] have been performed and have deduced barriers to rearrangements ranging from 0 to 27 kcal mol^{-1}. In general, there are discrepancies among the calculated results reported by various laboratories.[2] Experimental work on 1-aryl-2-diazopropanes has produced evidence in favor of a barrier to 1,2-H shift in dialkylcarbenes even though no value could be assigned.[8] In 1983, Lineberger and co-workers[9] examined the

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vibrational structure in the vinylidene photoelectron spectrum and suggested that there should be at least some barrier to hydrogen migration. Recently, the product from the thermolysis of 4-diazirinopentanoic acid allowed the estimate of an experimental value for $E_a = 1.1 \pm 1$ kcal mol^{-1} for the barrier height for 1,2-H shift in dialkylcarbenes.[10] The pioneering work of Moss and co-workers[11,12] demonstrated that cyclopropanation of olefins by diazirine-derived alkylhalocarbenes could be investigated with carbenes that undergo hydrogen migration. By examining the competitive inter- and intramolecular reactions of the carbenes, Liu and co-workers have recently obtained experimental values for the barriers in $PhCH_2\ddot{C}Cl$[13] and $PhCH_2\ddot{C}Br$[14] of 6.4 and 4.7 kcal mol^{-1}, respectively. We now report on the absolute rate constant for 1,2-hydrogen migration in benzylbromocarbene and the ambiphilic character of the carbene.

Experimental Section

General Method. The NMR spectra have been recorded on a Varian T-60 spectrometer with TMS as internal standard. GLC analysis of relative yields of products were performed on a Varian Vista 6000 gas chromatograph fitted with a 6 ft × 0.125 in. stainless steel column packed with CSP-20M and using a flame ionization detector. The GLC traces were calibrated by using authentic samples of the reaction products in each case. Peak areas were integrated with a Hewlett-Packard 3390A recorder.

Irradiation was carried out with 3500 UV lamps in a Rayonet photoreactor until all the diazirine (0.03 M in isooctane solution) was destroyed. Temperature control was within ±0.1 °C. 3-Bromo-3-benzyldiazirine was prepared by Graham's method[15] and purified by chromatography on silica gel. The absence of bromostyrene prior to photolysis was confirmed by NMR spectroscopy.

Product Studies. 3-Bromo-3-benzyldiazirine (2.5×10^{-3}/mol) was dissolved in 100 mL of approximately 1 M solution of alkene in isooctane and photolyzed at 5 °C for 4 h. The unreacted alkene and the solvent was distilled off under reduced pressure. The bromostyrenes and cyclopropane were analyzed by GLC. The residue was chromatographed over a column of silica gel (25 mm × 300 mm) and eluted with hexane and hexane containing 1–5% ethyl acetate. In every instance, the bromostyrenes were eluted in the first 250 mL of the solvent, and the subsequent fractions contained the cyclopropanes. The bromostyrenes were identified by comparison of their NMR spectra with those of authentic samples.[14] The cyclopropanes were characterized by means of NMR. Authentic samples of bromostyrenes and cyclopropane were used to calibrated the GLC. 1-Benzyl-1-bromo-2,2,3-trimethylcyclopropane: yield 27%; NMR ($CDCl_3$) δ 7.33 (s, 5 H, aromatic), 3.30 (s, 2 H, benzylic CH_2), 2.00 (s, H, cyclopropylmethine H), 1.26 (s, 6 H, cyclopropyl ring, 2-CH_3), 1.13 (s, 3 H, cyclopropyl ring CH_3). 1-Benzyl-1-bromo-2-*n*-butylcyclopropane: yield 20%; NMR ($CDCl_3$) δ 7.30 (s, 5 H, aromatic), 3.10 (s, 2 H, benzylic CH_2), 0.4–1.7 (m, 12 H, cyclopropyl ring and *n*-butyl H). 1-Benzyl-1-bromo-2-chloro-2-cyanocyclopropane: yield 45%; NMR ($CDCl_3$) δ 7.36 (s, 5 H, aromatic), 3.66 (s, 2 H, benzylic CH_2), 0.63–2.00 (m, 2 H, cyclopropyl H).

Laser Flash Photolysis. The LFP setup used a crossed-beam arrangements. The detection system includes a pulsed Xe arc, a monochromator, a red-sensitive photomultiplier (Hatmamatsu R446), and a fast transient recorder (Tektronix 7912) and has a response time around 5 ns. The sample cell (10 × 10 mm) is excited at 355 nm by single light pulses (200-ps duration, 5–30-mJ energy) provided by a frequency-tripled mode-locked Nd:YAG laser (Quantel).

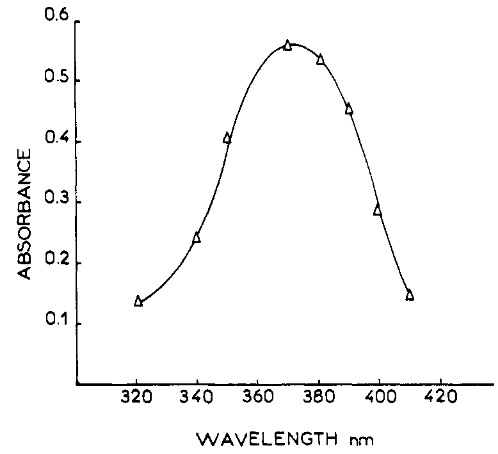


Figure 1. Point by point absorption spectrum for pyridinium ylide **3**, recorded at 25 °C in isooctane.

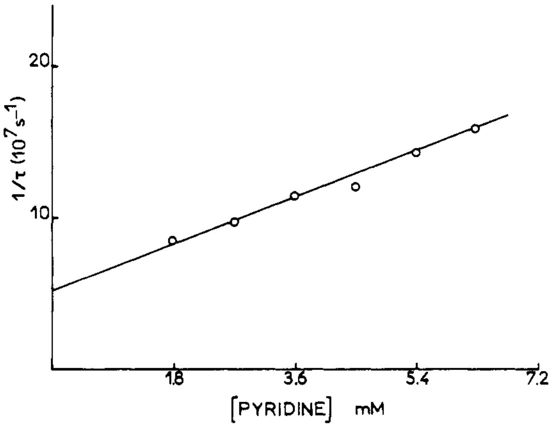
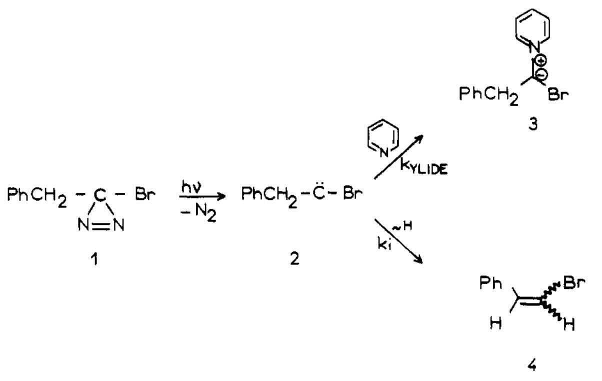


Figure 2. Pseudo-first-order rate constant ($1/\tau$) vs [pyridine] at 25 °C.

SCHEME I



Results and Discussion

Halodiazirines are effective precursors of halocarbenes in photochemical and thermal reactions.[16] Thus photolysis of 3-bromo-3-benzyldiazirine (**1**) generates benzylbromocarbene (**2**), which rearranges to a mixture of (*Z*)- and (*E*)-β-bromostyrenes. Carbene **2** has been demonstrated to have singlet ground state.[17] There have been many laser flash photolysis (LFP) studies on singlet arylhalocarbenes[16,18] mainly because their intense ab-

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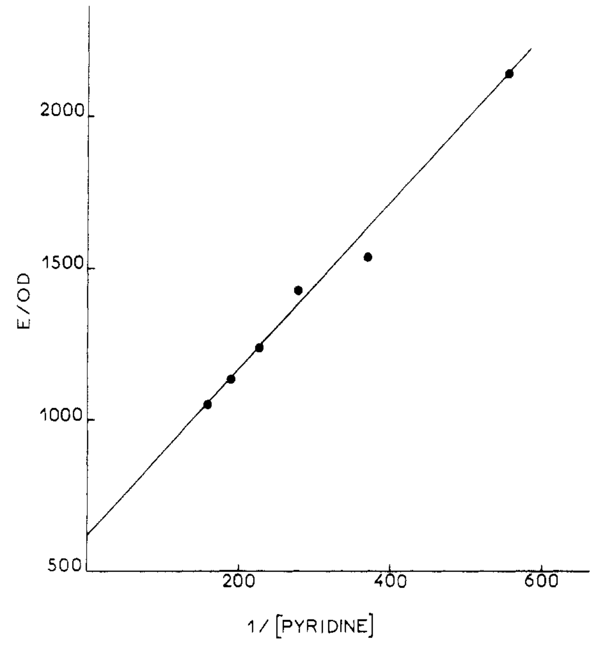


Figure 3. Plot of E/OD vs 1/[pyridine] at 25 °C.

sorption in the near-UV provides ideal probes to follow the dynamics of carbenes. LFP of 3-bromo-3-benzyldiazirine does not produce a transient spectrum for benzylbromocarbene (**2**) because of the lack of a suitable chromophore for its direct detection. Although several arylchlorocarbenes react with acetone to form carbonyl ylides,[19] the attempt to observe such an ylide with benzylbromocarbene was unsuccessful. However, LFP of **1** in isooctane at 25 °C in the presence of pyridine produces the transient spectrum shown in Figure 1. This transient is not present in the absence of pyridine and is attributed to the ylide **3**, as illustrated in Scheme I. Utilization of pyridinium ylide[20] as a probe (monitored at 370 nm) allows the measurement of the absolute rate constant for 1,2-H migration in benzylbromocarbene. A plot of the observed pseudo-first-order rate constant $1/\tau$ for the growth of ylide **3** vs [pyridine] is linear (Figure 2); the slope yields the absolute rate constant for reaction of $PhCH_2\ddot{C}Br$ with pyridine, $k_{ylide} = (1.59 \pm 0.09) \times 10^{10}\ M^{-1}\ s^{-1}$, and the intercept yields $k_i = (5.58 \pm 0.4) \times 10^7\ s^{-1}$ ($\tau \approx 18$ ns). Because the growth time of the ylide is near the rise time of our system for the higher concentrations of pyridine used in this study, the values for τ in Figure 2 have been determined by taking into consideration the response time of the system; i.e., $\tau^2 = (\tau_{obsd})^2 - (\tau_{system})^2$.

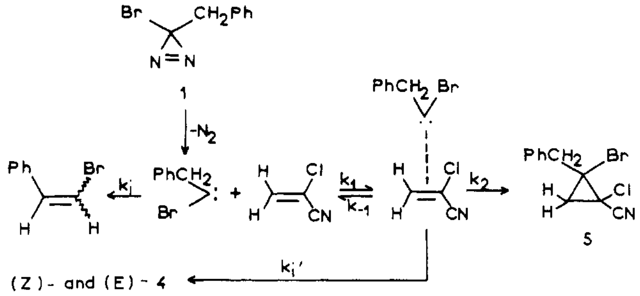
Since this correction is only empirical and the accuracy of extrapolated values is often questionable, it is possible to check the above kinetics data by a Stern–Volmer type analysis for the amount of ylide as a function of [pyridine]. The yield of ylide formation is given by $\phi_{ylide} = k_{ylide}\,[\text{pyridine}]/(k_i + k_{ylide}[\text{pyridine}])$ and the amount of carbene produced in a single pulse is [carbene] $= \alpha E$, where E is the reading of the energy meter monitoring the laser pulse intensity and α is a proportionality factor. The ylide absorption is OD = [ylide]ϵl, and it follows that

$$\frac{E}{\mathrm{OD}} = \frac{1}{\epsilon\alpha l} + \frac{k_i}{\epsilon\alpha l k_{ylide}}\,\frac{1}{[\text{pyridine}]} \qquad (1)$$

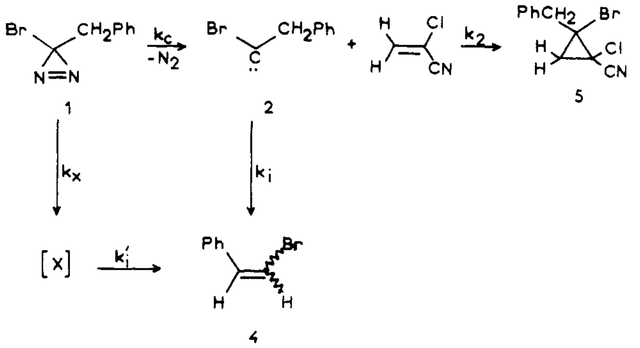
The intercept/slope ratio of the straight line plot E/OD vs 1/[pyridine] in Figure 3 gives $k_{ylide}/k_i = 246 \pm 37$, which compares quite well with the value 285 ± 36 obtained from the plot of $1/\tau$ vs [pyridine] in Figure 2.

In the second method, the response time of the analytical system is not important provided it is short compared to the decay time of the ylide, which is longer than a microsecond in our experimental conditions. It should be noticed that checking the value of k_{ylide}/k_i by the second method is a very efficient test of the first one. For instance, if there is a systematic error leading to large values of τ for the higher [pyridine], e.g., an underestimation of τ_{system}, this would not only give a too low value for k_{ylide} but also, by extrapolation, a too large value for k_i. Thus, the ratio k_{ylide}/k_i will decrease significantly and will rapidly become incompatible with the same ratio determined by the analysis of OD vs [pyridine].

SCHEME II



SCHEME III



At 25 °C, the A factor for an unimolecular process with zero entropy change is $10^{13.2}$, and assuming nearly one degree of rotational freedom is lost (hence $\Delta S^* = -3.7$ eu) during the H migration, we may estimate $A_i = 10^{12.6}$ and calculate $E_i = 6.6$ kcal mol^{-1} for the 1,2-H migration process. In our competitive inter- and intramolecular studies on benzylbromocarbene, we reported an activation energy of 4.7 kcal mol^{-1} for the above process. Considering that the intermolecular rate for addition of $PhCH_2\ddot{C}Br$ to tetramethylethylene (TME) was assumed to be equal to that measured for the system $Ph\ddot{C}Br$ + TME, the agreement is very good.

Recent work on the addition of phenylchlorocarbenes to α,β-unsaturated systems indicates that the reaction occurs with remarkable facility.[21] Frontier molecular orbital analysis establishes the necessity of including a nucleophilic term in estimating the stabilization energy of the transition state for additions of these carbenes with electron-deficient olefins. In an attempt to understand the philicity of benzylbromocarbene, we examined the decomposition of 3-bromo-3-benzyldiazirine in the presence of various alkenes, in particular α-chloroacrylonitrile, which was introduced by Moss, Krogh-Jespersen, and co-workers[22] as an excellent detector substrate for nucleophilic and ambiphilic carbenes.

Photolysis of 0.02 M of **1** in the presence of excess alkene yields (Z)- and (E)-β-bromostyrene (**4**) and cyclopropanes **5**. The alkene substrates used in the present experiments were 1-hexene (HEX), α-chloroacrylonitrile (ClACN), and 2-methyl-2-butene (M3E). The **5**/**4** product ratios were determined as a function of alkene concentrations, but the effect of temperature was studied only for the case of ClACN. The results are given in Table I. In general, the intermolecular/intramolecular product ratio (**5**/**4**) does not

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TABLE I: Product Distribution of the Photolysis of 1 in ClACN (Isooctane Solvent)

	5.1 °C		15.1 °C		27.2 °C		45.5 °C	
[ClACN], M	Z/E	**5/4**	Z/E	**5/4**	Z/E	**5/4**	Z/E	**5/4**
0.22	0.48	0.455	0.43	0.330	0.30	0.225	0.23	0.122
0.41	0.48	0.617	0.43	0.461	0.30	0.318	0.23	0.186
0.83	0.50	0.739	0.46	0.552	0.35	0.382	0.24	0.269
1.23	0.50	0.759	0.46	0.631	0.40	0.470	0.29	0.288
1.61	0.52	0.800	0.48	0.636	0.42	0.497	0.33	0.324
1.95	0.54	0.826	0.50	0.667	0.44	0.501	0.36	0.327
2.34	0.60	0.840	0.50	0.638			0.39	0.324
2.80	0.60	0.828	0.52	0.663	0.45	0.500	0.41	0.350
k_i/k_t	0.236 ± 0.008		0.363 ± 0.01		0.588 ± 0.03		1.25 ± 0.03	
k_i'/k_2	1.096 ± 0.015		1.347 ± 0.025		1.724 ± 0.046		2.383 ± 0.060	

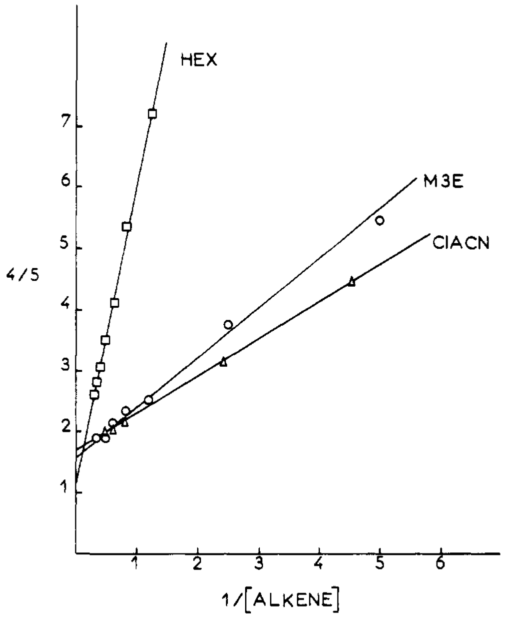

Figure 4. Plots of bromostyrene/cyclopropane vs 1/[alkene].

reflect the ratio of the intermolecular/intramolecular rates since the ratios **5**/**4** vs alkene concentrations are not linear. To account for the observed results, two mechanistic models (Schemes II and III) can be proposed in which two parallel routes to the formation of **4** are operative. In Scheme II, the carbene–alkene complex is assumed to be weakly bound, formed at long distances, so that the dissociation (k_{-1}) can compete with the formation of products (k_i', k_2). Such a complex has been proposed for the addition of phenylchlorocarbene[18] and benzylchlorocarbene[13] to alkenes. Steady-state treatment in Scheme II leads to

$$\frac{\mathbf{4}}{\mathbf{5}} = \frac{k_i'}{k_2} + \frac{k_i}{k_t}\frac{1}{[\text{alkene}]} \tag{2}$$

where the overall cyclopropanation rate constant k_t is equal to $k_1k_2/(k_{-1} + k_i' + k_2)$. Scheme III, regardless of the nature of the X intermediate,[23] leads to an analytically similar expression

$$\frac{\mathbf{4}}{\mathbf{5}} = \frac{k_x}{k_c} + \frac{(k_x + k_c)}{k_c}\frac{k_i}{k_2}\frac{1}{[\text{alkene}]} \tag{3}$$

In both cases, the plot of **4**/**5** vs 1/[alkene] should be linear with a nonzero intercept. Such linear plots are indeed obtained for the various alkenes (Figure 4) as well as for experiments performed with ClACN at various temperatures (Figure 5). It should be noted that the above plots have different intercepts and that similar variations have been observed in the case of benzylchlorocarbene.[13] According th eq 2, the intercept is equal to k_i'/k_2. This ratio is a characteristic of the complex and will depend on the nature of the alkene. The variation of the intercept with temperature is easily rationalized if k_2 and k_i' have different temperature dependence. In eq 3, on the other hand, the intercept, k_x/k_c, is a characteristic of the excited diazirine. This ratio should be independent of the alkene, and it is also likely to be independent of the temperature. This is clearly not the case and Scheme III can be discarded on this basis. The values of k_i/k_t and k_i'/k_2 for the four temperatures (Table I), with error limits quoted as the standard deviations, were obtained by least-squares analysis of the slope and intercept of the straight lines shown in Figure 5. An Arrhenius plot of these values (ln (k_i/k_t) and ln (k_i'/k_2) vs $1/T$) gives

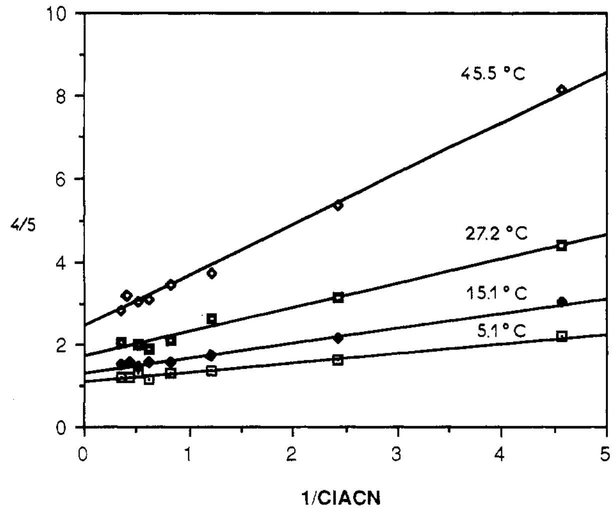

Figure 5. Plots of bromostyrene/cyclopropane vs 1/[ClACN] as a function of temperature.

$$E_i - E_t = 7.33 \pm 0.17 \text{ kcal mol}^{-1} \quad \text{and} \quad A_i/A_t = 10^{5.1\pm0.13}$$

$$E_i' - E_2 = 3.40 \pm 0.02 \text{ kcal mol}^{-1} \quad \text{and} \quad A_i'/A_2 = 500 \pm 20$$

With the values of E_i and A_i estimated above, 6.6 kcal mol^{-1} and $10^{12.6}$, respectively, the kinetic parameters for the cycloaddition of $PhCH_2\ddot{C}Br$ to ClACN are

$$A_t = 10^{7.5} \quad \text{and} \quad E_t = -0.73 \text{ kcal mol}^{-1}$$

Assuming that E_i' and A_i' are nearly equal to E_i and A_i, i.e., the kinetic parameters for the 1,2-H transfer are very similar in the free carbene and in the loose carbene–alkene complex, it follows that

$$A_2 = 10^{9.9} \quad \text{and} \quad E_2 = 3.2 \text{ kcal mol}^{-1}$$

Recall that $k_t = k_1k_2/(k_{-1} + k_i' + k_2)$. At room temperature, the value for $k_t \approx 10^8$ (from the slope and k_i values) and $k_i' = 1.6\,k_2$ (from the intercept). With $k_1 = k_{\text{diff}} = 2 \times 10^{10}$ M^{-1} s^{-1}, one gets $k_{-1} = 76(k_i' + k_2)$ so that k_t can be reduced to k_2k_1/k_{-1}. If $k_i' = k_i$, $k_{-1} \approx 7 \times 10^9$ and the equilibrium constant for the formation of the complex is approximately 3. This low value supports the weak bonding character which has been assigned to the complex and the assumption that the kinetic parameters for the 1,2-H transfer in the free and complexed carbene are similar.

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(23) X could be a diazo intermediate or an excited carbene as suggested by: Warner, P. M. *Tetrahedron Letter.* **1984**, *25*, 4211.

TABLE II: Product Distribution in the Photolysis of 1 in 1-Hexene and 2-Methyl-2-butene at 25 °C (Isooctane Solvent)

[HEX]	5/4	[M3E]	5/4
0.4	0.077	0.2	0.184
0.8	0.139	0.4	0.265
1.2	0.187	0.8	0.398
1.6	0.243	1.2	0.427
2.0	0.285	1.6	0.471
2.4	0.325	2.0	0.524
2.8	0.361	2.4	0.522
3.2	0.384	2.8	0.531
k_i/k_t	4.76 ± 0.06		0.779 ± 0.024

TABLE III

	TME	M3E	HEX	ClACN
k_i/k_t	0.91	0.78	4.76	0.556
k_{rel}	5.5	6.0	1.0	8.5
π-ME	3.0	3.22	3.84	5.46

By employing the same method, the kinetic parameters for the cycloaddition of $PhCH_2\ddot{C}Br$ to TME can be calculated from previously published data.[14]

$$A_t = 10^{8.2} \quad \text{and} \quad E_t = 0.4 \text{ kcal mol}^{-1}$$

$$A_2 = 10^{10.5} \quad \text{and} \quad E_2 = 4 \text{ kcal mol}^{-1}$$

The similarity of the activation parameters for the two sets of totally electronically different alkenes vitiates any distinction between benzylbromocarbene reactions toward electron-rich and electron-poor alkenes.

Results from the photolysis of **1** with 1-hexene and with 2-methyl-2-butene in isooctane are given in Table II. Values for k_i/k_t were derived in similar manner. The relative cyclopropanation rate constants (k_{rel}) derived from k_i/k_t ratios for $PhCH_2\ddot{C}Br$ in isooctane at 25 °C are given in Table III.

The π-molecular electronegativity (π-ME; Table III) of the alkene can be calculated[21] from (IP + EA)/2, the average of its π and π^* orbital energies as approximated by IP and EA values. The U-shaped behavior of k_{rel} vs π-ME indicates that the rate increases at both ends where electrophilic LUMO(carbene)/HOMO(alkene) and nucleophilic HOMO(carbene)/LUMO(alkene) interaction became pronounced. Similar parabola was observed for $PhCH_2\ddot{C}Cl$.[24] Our present results suggest that benzylbromocarbene, like benzylchlorocarbene, is an ambiphile and can be induced to react as a nucleophile in the presence of electron-poor olefins.

The 1,2-H migration produces (*Z*)- and (*E*)-β-bromostyrene in a ratio that is dependent on the concentration and on the structure of the alkenes. An increase in *Z*/*E* ratio with increase in cyclopropanation is generally observed except in the case of 1-hexene where the *Z*/*E* ratios remain unchanged when [1-hexene] is increased. This could be related to the fact that cyclopropanation with 1-hexene does not compete well with 1,2-H migration. In the case of TME, M3E, and ClACN, the changes in *Z*/*E* ratios follow closely the changes in **5**/**4** values in a manner that there is no further change in *Z*/*E* when the **5**/**4** ratio reaches a limiting values. A similar observation[25] indicating increased *Z*/*E* ratios with increase in the extent of cycloaddition can be seen in the reaction of para-substituted benzylchlorocarbenes with (*Z*)-4-methyl-2-pentene (0.15, 0.26, 0.34, 0.44 for MeO, Me, H, and Cl, respectively). This can be easily explained by considering the mechanism proposed in Scheme II by assuming that the *Z*/*E* ratio is not the same for the β-bromostyrene produced by the 1,2-H migration in the free carbene and in the complex.

In spite of tremendous efforts to understand the behavior of the arylhalocarbene–alkene reactions by laser flash photolysis,[16,18,21] there are no definite conclusions primarily because the carbene–alkene complexes have yet to be directly observed. Our present kinetic data are best explained in terms of such a carbene–alkene intermediate.

Registry No. **1**, 69967-70-0; **2**, 99281-00-2; **3**, 120524-11-0; (*Z*)-**4**, 588-73-8; (*E*)-**4**, 588-72-7; **5**, 120524-12-1; HEX, 592-41-6; M3E, 513-35-9; $CH_2{=}CClCN$, 920-37-6.

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Characterization of Oscillatory States in the Electrochemical Oxidation of Formaldehyde and Formate/Formic Acid

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The oscillatory response of the potential was monitored in two electrochemical reactions carried out under galvanostatic conditions. In the oxidation of formaldehyde, incrementing the current generated a sequence of temporal states consisting of alternating intervals of periodic and chaotic behaviors. A sequence of periodic states, which obeys Farey addition, was found in the oxidation of formate/formic acid. The temporal states in both reactions consisted of different combinations of small and large oscillations. The observation of these mixed oscillations implies that the kinetic mechanisms contain at least two coupled instabilities.

Introduction

There is a renewed interest in electrochemical oscillations that can partly be attributed to the fact that techniques developed in nonlinear chemical dynamics[1] are now available for the purpose of identifying different oscillatory behaviors. The application of these techniques has recently led to the characterization of several different temporal states and bifurcations between these states in electrochemical processes. Some examples include chaos,[2-7]

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