TIME-RESOLVED FLASH SPECTROSCOPIC INVESTIGATIONS OF THE REACTIONS OF SINGLET ARYLHALOCARBENES

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Abstract—The results of time-resolved laser flash spectrometric studies of singlet arylhalocarbenes are reviewed. In particular, the absolute rate constants for reactions of phenylchlorocarbene and related carbenes with alkenes are summarized and systematized. The experiments described provide the basis for a detailed examination of carbenic reactivity–selectivity principles. The results of studies on the influence of temperature on the absolute rate constants for carbene reactions are consistent with the existence of transient carbene/alkene intermediates.

Since the renaissance of carbene chemistry, a great deal has been learned concerning the mechanisms of reaction of these species.[1,2] In these studies, kinetic measurements have played an important role in our understanding of the reaction processes. In particular, the establishment of the carbenic selectivity index (or m_{CXY} value) has allowed the standardization of relative reactivity parameters, so that these types of measurements have become the method of choice for the majority of carbene chemists working in this field.[2,3a] The m value for a particular carbene is determined from a plot of the logarithm of the relative reactivities of that carbene toward a standard set of olefins, against corresponding data for the "standard" carbene, dichlorocarbene.[3a] If the slope of such a plot (the m value) is less than unity, then that carbene has a smaller spread of relative rates than the standard and is thus considered to be less selective. Carbenes with m values greater than unity are more selective than dichlorocarbene. It is usually assumed that the normal reactivity–selectivity relationship holds, i.e. that the less selective carbenes are the more reactive.[3b,c] However, there has been a remarkable dearth of absolute kinetic studies on carbene reactions. Although the reactions are too fast to be measured using conventional techniques, the advent of pulsed laser spectroscopy has provided carbene chemists with a powerful new tool for the investigation of these reactions.[4] The central experiment consists of fast formation of a carbene using a short laser pulse, and subsequent direct observation of the carbene by means of its optical absorption. In this manner the absolute reactivities of diphenylcarbene,[5] fluorenylidene,[6] and 1-naphthylcarbene[7] have been investigated. These studies have allowed a new insight into the reactions of these transient species, although, as in conventional experiments, the problem of carbene multiplicity has arisen.[8] In the present work we describe the results of our studies on the reactivity of a series of phenylhalocarbenes toward a variety of olefinic quenchers.[9] For these carbenes only the reactions of the singlet state need to be considered (*vide infra*). The main thrust of the work has been to investigate the reactivity–selectivity relationship of these intermediates using absolute kinetic measurements, and to determine what new information can be obtained using the time-resolved techniques. Two other investigations of the absolute reactivity of phenylchlorocarbene have been reported. Scaiano and Griller have examined its reactivity toward alcoholic substrates and have found evidence for differing reactivity of methanol monomers and oligomers.[10a] The same workers have also investigated the reactions of phenylchlorocarbene with carboxylic acids.[10b]

Pulsed laser photolysis

The pulsed laser photolysis technique relies on the premise that the timescale for formation of the species under investigation is much shorter than the lifetime of that species. In general, conditions can be found such that photolysis of a carbene precursor yields the carbene "instantaneously", i.e. within the time period of the pulse. The pulse width used in the present work is 15 ns, so that transient species with lifetimes $\geqslant$ 50 ns can be easily analyzed. The transient carbenes are detected by means of their optical absorptions. The detection system consists of a Xenon arc lamp which is focused through the quartz glass sample cell (Fig. 1) and then by means of lenses onto the entrance slit of a monochorometer. The transmitted light intensity which leaves the cell is monitored using a photomultiplier tube (PMT). The monochrometer is used to select light at a wavelength where the carbene absorbs. The laser light is focused so that the excitation and monitoring beams overlap within the sample cell (Fig. 1). After the laser has fired, the transmitted light intensity is decreased due to the formation of the carbene (which occurs within the laser pulse). As the carbene reacts (decays) the transmitted light intensity "recovers" with a time constant equal to that of the carbene lifetime. The transmitted light which is incident on the PMT causes a current to flow within this device. The current is detected as a voltage, which is directly

proportional to the incident light intensity, across a load resistor which is placed in series with the PMT output. The voltage waveform is recorded as a function of time using a digital oscilloscope and is transferred to a small computer for analysis. The computer converts the transmitted light intensity into optical density, which is directly related to concentration of the transient species, as a function of time. A representative oscilloscope trace, together with the results of the data manipulation, are shown in Fig. 2. Typically 1×10^{-5} mol of transient species are formed within the pulse, and thus the transient must have an extinction coefficient $\varepsilon \geqslant 1000$ for routine detection. From the concentration versus time data, the kinetic order of the transient decay and the lifetime of the transient follow directly.

RESULTS

Photolysis of phenylchlorodiazirine

Steady-state photolysis of phenylchlorodiazirine (1a) generates phenylchlorocarbene (2a) which, in the presence of tetramethylethylene (3), isobutene (4),

$= 351$ nm) of 1a in isooctane at room temperature gives rise to strong transient absorption signals in the region 290–340 nm, which appear within the time period of the laser pulse. Analysis of the signal as a function of wavelength allows construction of the transient spectrum shown in Fig. 3. The λ_{max} which is observed at room temperature is in good agreement with that found at 77 K. The lifetime of the transient species monitored at 320 nm in homogeneous solution at room temperature, is independent of the concentration of dissolved oxygen. Although irradiation of 1a in a glass at 77 K results in strong optical absorptions, no ESR signal can be detected from the sample.[12] The transient absorption signals are therefore assigned to phenyl-chlorocarbene which is assumed to possess a ground singlet state because of its stereospecific addition reactions,[11] the lack of an oxygen effect on its lifetime, and the lack of an ESR signal.

### Reaction with and quenching by olefins

Generation of 2a in binary alkene mixtures, followed by quantitative HPLC analysis and standard relative

1a X = H
1b X = CF₃
1c X = Cl
1d X = Me
1e X = OMe

3

4

5

6

7
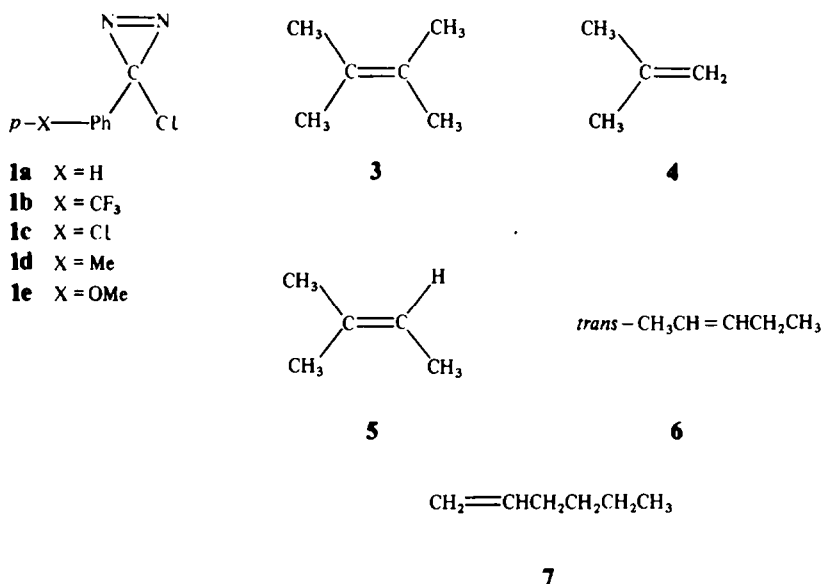
trimethylethylene (5), trans-2-pentene (6) or 1-hexene (7) leads to clean production of cyclopropane products (Eqn 1).[11] Previous work has shown this addition reaction to be stereospecific with 2-butenes.[11]

rate analysis[3a] of the cyclopropane products allowed determination of the relative rates for product formation for each of the olefins (Table 1).

Laser photolysis of 1a in isooctane in the absence of

(1)

2a X = H
2b X = CF₃
2c X = Cl
2d X = Me
2e X = OMe
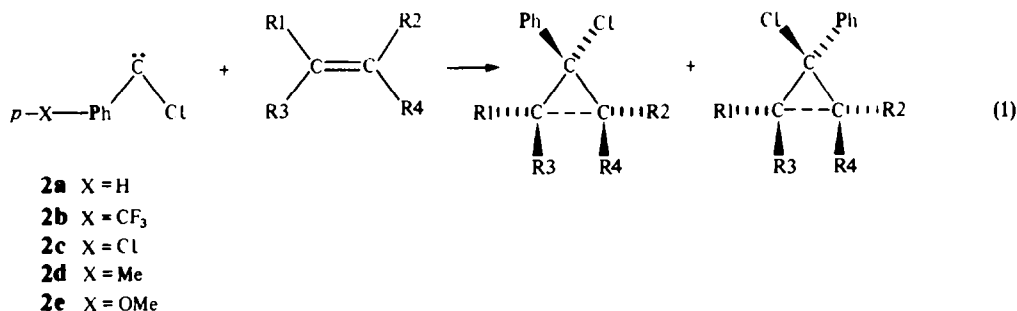
Photolysis of 1a ($\lambda > 300$ nm) in a 3-methylpentane glass at 77 K yields a strong optical absorption signal with $\lambda_{max} = 307$ nm (Fig. 3), which is stable at 77 K, but disappears upon annealing. Pulsed laser photolysis (λ_{ex}

quenchers leads to clean second order decay of the carbene signal observed at 320 nm, presumably due to dimerization. Upon addition of olefin the lifetime of the carbene decreases due to quenching of this species by
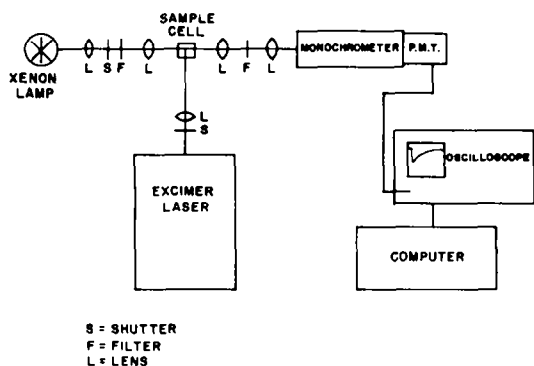
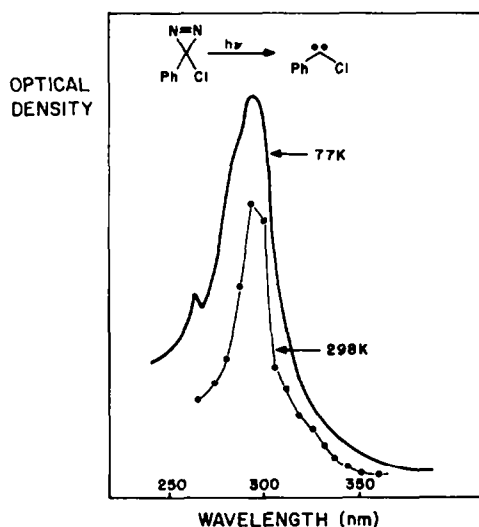Fig. 1. Diagrammatic representation of the laser flash photolysis apparatus.

Fig. 3. Absorption spectrum of phenylchlorocarbene in a 3-methylpentane glass at 77 K and in isooctane at room temperature, in arbitrary optical density units.

the olefin. In the presence of a sufficient concentration of the quencher the carbene decay becomes pseudo-first order, and a plot of the pseudo-first order rate constant for decay versus the olefin concentration in this region yields the bimolecular quenching rate constant (k_{abs}) as the slope. The values of k_{abs} for the reaction of **2a** with four olefins in isooctane, determined in this manner, are given in Table 1. Relative rate constants calculated from the absolute rate data are in reasonable agreement with those obtained from the steady-state competition experiments. These results imply that the observed absolute rates of quenching refer to the rates for cyclopropane product formation, and support the assignment of the transient absorption.

Effect of substituents

Photolysis of the diazirines **1b–e** in a manner analogous to that of the parent compound produces the corresponding *para*-substituted carbenes. Production of the carbenes in binary olefin mixtures as before allowed the determination of the relative rate constants
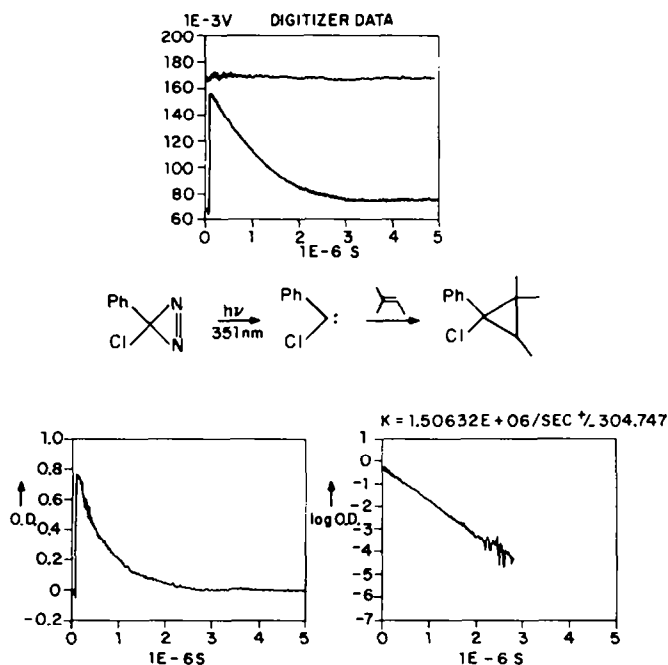
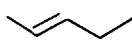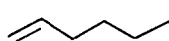TRANSIENT DIGITIZER GRAPHICS OUTPUT

Fig. 2. Typical computer output showing (top) transmitted light intensity as a function of time, (bottom left) optical density of the carbene as a function of time, and (bottom right) semilog plot for first order carbene decay, for photolysis of phenylchlorodiazirine in the presence of trimethylethylene in isooctane at room temperature.

Table 1. Rate constants* for the additions of phenylchlorocarbene to alkenes

| Alkene	k_{abs} (1 mol^{-1} s^{-1})	k_{rel}^{abs}†	k_{rel}^{comp}§
(structure)	2.8×10^8	1.00	1.00
(structure)	1.3×10^8	0.46	0.62
(structure)	5.5×10^6	0.020	0.028
(structure)	2.2×10^6	0.0079	0.012

* Experimental error is ±10%.
† Relative rates calculated from absolute rate data.
§ Relative rate data determined from steady-state competition experiments.

for reactions of each carbene with olefins 3, 4, 6 and 7 as shown in Table 2. In each case cyclopropanes were the only detected products.

Similarly, pulsed laser photolysis of the diazirines in the presence of the four olefins in isooctane allowed determination of the absolute rate constants (Table 3). Again the relative rate data from the two experiments support the conclusion that the absolute rate constants reflect the rates of cyclopropane formation, although some deviations are noted, particularly for the slower reactions (Table 2 and below). It is observed that electron withdrawing groups on the carbene increase the absolute rate of addition, whereas electron donating groups on the carbene retard the reaction.

The effect of substituents on the olefin quencher was examined by determining the absolute quenching behavior of the substituted styrenes 8a–d. The absolute rate constants for quenching of the carbenes 2a–e by the four styrenes are given in Table 4. In this case, we again observe that electron withdrawing groups on the carbene accelerate the addition reactions (with each

$$p-X\text{——}Ph\text{——}CH\text{=}CH_2$$
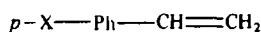
8a   X = Cl
8b   X = H
8c   X = Me
8d   X = OMe

styrene), just as they did for the olefins 3 and 5–7 (Table 3). We also note that for p-CF$_3$ and p-Cl substituted phenylchlorocarbenes, substitution of electron donating groups on the styrenes accelerates the additions (Table 4). However, with p-MeO, p-Me and unsubstituted phenylchlorocarbenes, p-chlorostyrene reacts more rapidly than styrene or even p-methylstyrene.

We also examined the effect of substitution at the carbene center. Thus photolysis of phenylbromodiazirine (9) and phenylfluorodiazirine (10) in the

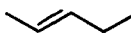(structures 9 and 10)
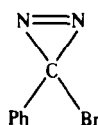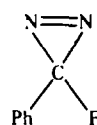
9   **10**

presence of the olefins 3 and 5–7 gives rise to clean cyclopropane formation. The absolute rate constants for reactions of the three phenylhalocarbenes (2a, 11 and 12) with the four olefins are summarized in Table 5.

(structures 11 and 12)
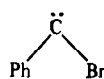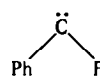
11   **12**

For each olefin the order of carbenic reactivity is Br > Cl > F. For each carbene, the order of olefinic reactivity is 3 > 5 > 6 > 7.

Finally the effect of solvent on the absolute rate constant for the reaction of 2a with 3 was investigated. The rate constants for this reaction in isooctane,
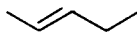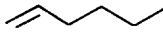
Table 2. Relative rate data* for the reactions of the phenylchlorocarbenes 2a–e with alkenes 3, 4, 6 and 7†

Alkene	*para*-substituent on the carbene				
	CH$_3$O	Me	H	Cl	CF$_3$
(structure)	1.00	1.00	1.00	1.00	1.00
(structure)	0.37	0.26	0.25	0.22	0.24
(structure)	0.038 (0.031)	0.028 (0.015)	0.028 (0.020)	0.029 (0.023)	0.033 (0.033)
(structure)	0.017 (0.0093)	0.012 (0.0052)	0.012 (0.0079)	0.012 (0.0070)	0.012 (0.012)

* Experimental error is ±2%.
† Values in parentheses are relative rate data calculated from absolute rate constants (see Table 3).

Table 3. Absolute rate constants* $(1 \text{ mol}^{-1} \text{ s}^{-1})$ for the reactions of the phenylchlorocarbenes **2a–e** with alkenes 3 and 5–7

Alkene	para-substituent on the carbene					ρ†
	CH_3O	Me	H	Cl	CF_3	
(alkene structure)	1.4×10^7	1.2×10^8	2.8×10^8	3.3×10^8	1.5×10^9	1.5
(alkene structure)	7.7×10^6	4.9×10^7	1.3×10^8	1.8×10^8	6.8×10^8	1.4
(alkene structure)	4.4×10^5	1.8×10^6	5.5×10^6	7.5×10^6	4.9×10^7	1.5
(alkene structure)	1.3×10^5	6.2×10^5	2.2×10^6	2.3×10^6	1.8×10^7	1.6
"spread"§	(108)	(194)	(127)	(143)	(83)	

* Experimental error is ±10%.
† Slopes of Hammett plots (see Fig. 9).
§ Ratios of rate constants for reaction with alkene 3 versus alkene 7.

acetonitrile, and toluene are given in Table 6. Only a small solvent effect was observed.

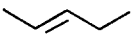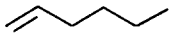*Temperature effects*

In order to determine whether the observed reactivity trends were due to enthalpic or entropic effects, the temperature dependencies of the carbene/alkene absolute rate constants were investigated.[13] Arrhenius plots for the reaction of **2a** with the olefins 3 and 5–7 are given in Fig. 4. Corresponding plots are shown for reactions of **2b** and **2e** with 3 in Fig. 5, and for reactions of 11 and 12 with 3 and 7 in Fig. 6. The effect of solvent on the Arrhenius plots is shown in Fig. 7 for reaction of **2a** with 3 in acetonitrile and toluene. The most striking feature of the plots is that negative slopes and nonlinear behavior are observed for the fastest reactions.

Spectroscopy of the carbenes

Photolysis of each of the diazirines in a 3-methylpentane glass at 77 K results in strong absorptions in the wavelength range 250–370 nm due to formation of the corresponding carbenes. In Fig. 8 are shown the absorption spectra of carbenes **2b–e**, and in Fig. 9 are the spectra of carbenes **2a, 11** and 12. The spectral data are summarized in Table 7. In each case,

Table 5. Absolute rate constants* $(1 \text{ mol}^{-1} \text{ s}^{-1})$ for the reactions of phenylchloro-, phenylbromo- and phenylfluorocarbenes with alkenes 3 and 5–7 in isooctane

Alkene	Carbene		
	FCPh	ClCPh	BrCPh
(alkene structure)	1.6×10^8	2.8×10^8	3.8×10^8
(alkene structure)	5.3×10^7	1.3×10^8	1.8×10^8
(alkene structure)	2.4×10^6	5.5×10^6	1.2×10^7
(alkene structure)	0.93×10^6	2.2×10^6	4.0×10^6
m_{CXY}†	0.89	0.83	0.70
"spread"§	172	127	95

* Experimental error is ±10%.
† Carbenic selectivity index from relative rate studies (ref. 3a).
§ Absolute rate constant ratio for carbene addition to 3 versus 7.

Table 4. Absolute rate constants* $(1 \text{ mol}^{-1} \text{ s}^{-1})$ for the reactions of the phenylchlorocarbenes **2a–e** with styrenes **8a–d** in isooctane

Carbene	para-substituent on the styrene			
	Cl	H	Me	MeO
p-CF₃PhCCl	2.0×10^8	3.0×10^8	4.6×10^8	6.5×10^8
p-ClPhCCl	6.0×10^7	7.1×10^7	1.1×10^8	2.9×10^8
PhCCl	4.4×10^7	4.0×10^7	4.3×10^7	1.3×10^8
p-MePhCCl	2.7×10^7	1.8×10^7	2.2×10^7	1.3×10^8
p-MeOPhCCl	8.8×10^6	3.7×10^6	4.5×10^6	1.2×10^8

* Experimental error is ±10%.

Table 6. Absolute rate constants* $(1 \text{ mol}^{-1} \text{ s}^{-1})$ for the reactions of phenylchlorocarbene with tetramethylethylene in isooctane, acetonitrile or toluene at room temperature

Solvent	k_{abs}
Isooctane	2.8×10^8
Acetonitrile	1.1×10^8
Toluene	1.4×10^8

* Experimental error is ±10%.
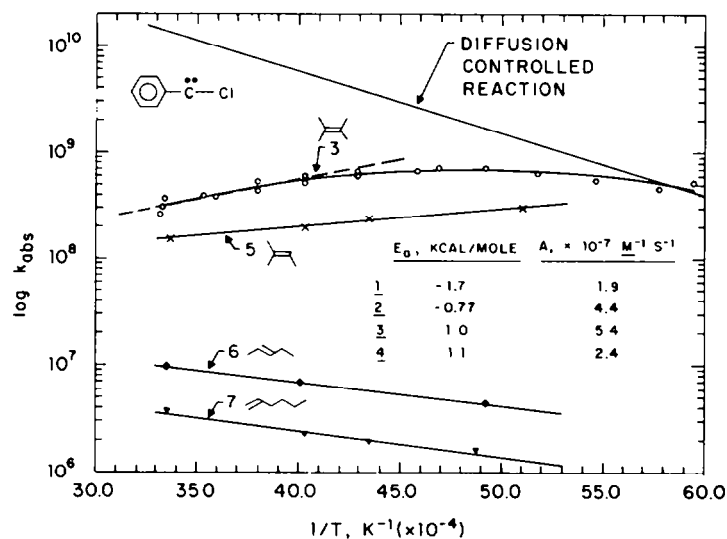
Fig. 4. Arrhenius plots for the reactions of phenylchlorocarbene with olefins **3, 5, 6** and **7** in isooctane.
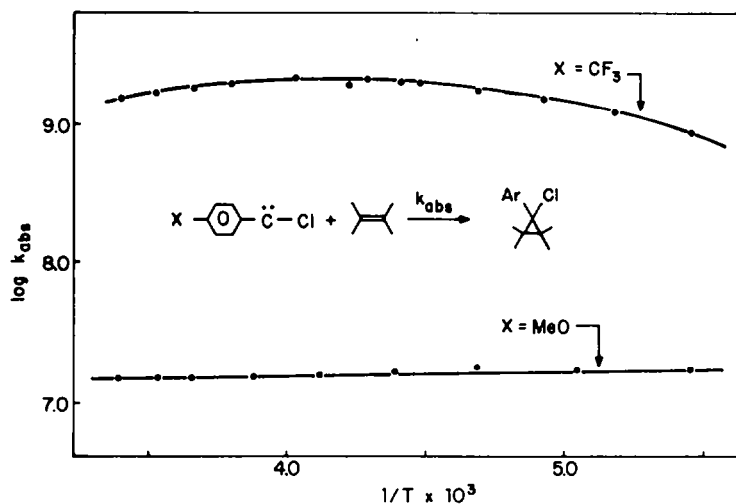

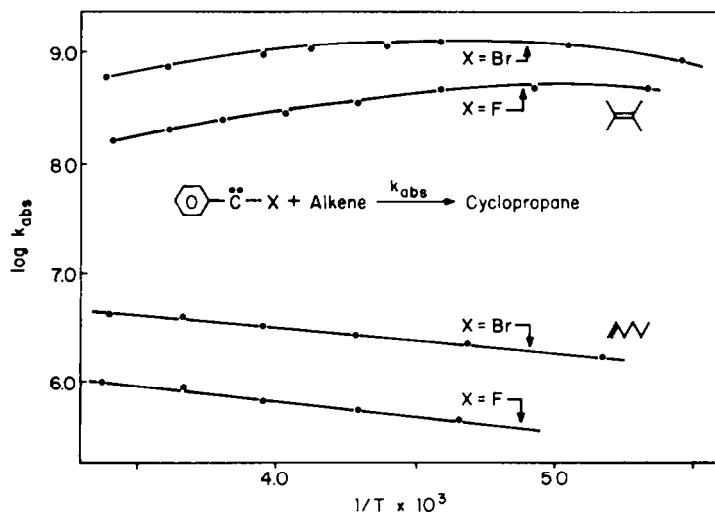Fig. 5. Arrhenius plots for the reactions of carbenes **2b** and **2e** with tetramethylethylene in isooctane.

Fig. 6. Arrhenius plots for the reactions of phenylbromocarbene (**11**) and phenylfluorocarbene (**12**) with tetramethylethylene and 1-hexene in isooctane.
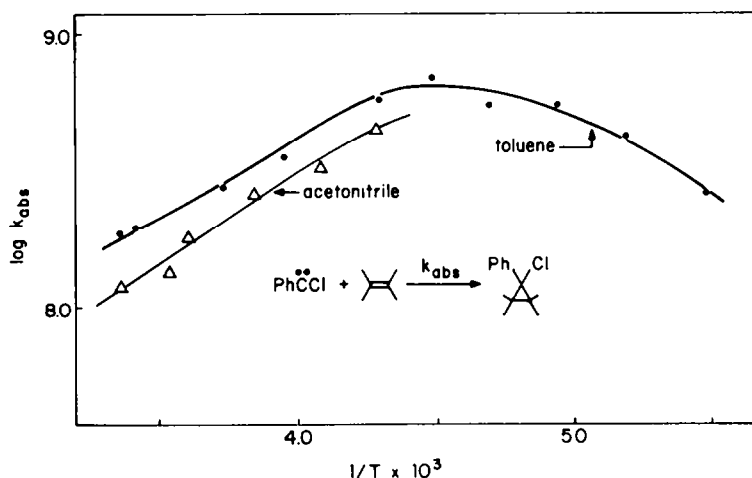
Fig. 7. Arrhenius plots for the reactions of phenylchlorocarbene with tetramethylethylene in acetonitrile and toluene.

good agreement is observed between the low temperature spectra and point-by-point spectra determined at room temperature using pulsed laser photolysis. Also given in Table 7 are the minimum extinction coefficients of the absorption bands for the spectra determined at 77 K. These were determined by photolyzing a known concentration of diazirine starting material, at a wavelength where only the diazirine absorbed, until a maximum optical density due to carbene was observed. The extinction coefficients were obtained from the optical densities of the carbene absorption bands and the concentrations of the starting material. These are minimum values because it is not known whether all of the diazirine is converted to carbene at the end of the irradiation. The extinction coefficients are all within 1 order of magnitude of a common value, which implies that each refers to the same type of transition.

Also given in Table 7 are the wavelengths at which the kinetic analysis of each carbene were performed. This is not necessarily the wavelength of maximum absorbance because most of the experiments were performed with monitoring at the wavelength of least absorbance by the parent diazirine. The carbene absorbances were so strong that sufficient transient absorption for routine analysis was observed at these selected wavelengths.

DISCUSSION

Comparison of relative and absolute rate constants

The purpose of the determination of both relative and absolute rate constants was to establish with confidence that the observed transient species were indeed the carbenes and that the observed absolute rate constants accurately reflected the rates of cyclopropane formation. The data convincingly support the first conclusion and, in the main, also support the second. Some differences between the absolute and relative rate data are observed for the slower reactions in Table 2. As
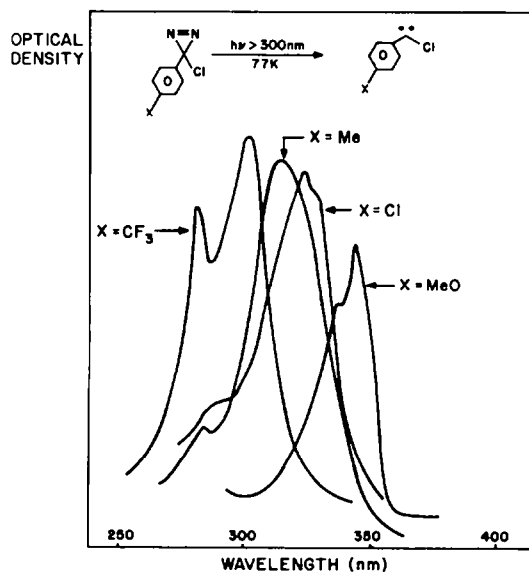

Fig. 8. Absorption spectra of the carbenes 2b–e in 3-methylpentane at 77 K in arbitrary optical density units.
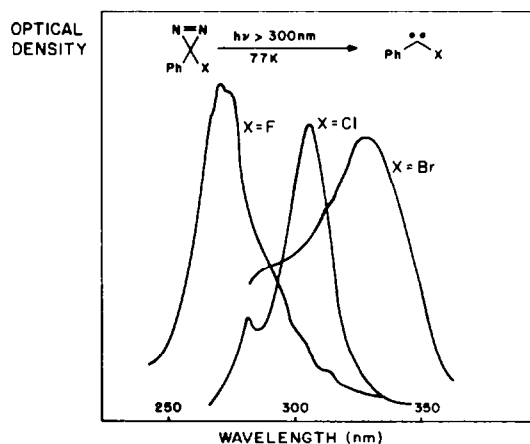

Fig. 9. Absorption spectra of phenylchlorocarbene (2a), phenylbromocarbene (11) and phenylfluorocarbene (12) in 3-methylpentane at 77 K in arbitrary optical density units.

Table 7. Absorption maxima of phenylhalocarbenes in 3-methylpentane at 77 K and in isooctane at room temperature

| Carbene | 77 K* | | R.T.† | |
	max§	min‖	max¶	obs**
PhCCl (2a)	307	1.2×10^4	310	320
	[282	4.2×10^3]		
p-CF$_3$PhCCl (2b)	303	9.4×10^3	298	320
	[292	7.8×10^3]		
p-ClPhCCl (2c)	323	4.6×10^3	320	320
	[291	1.5×10^3]		
p-MePhCCl (2d)	317	6.3×10^3	317	320
	[285	1.9×10^3]		
p-MeOPhCCl (2e)	346	4.0×10^4	340	330
	[339	3.3×10^4]		
PhCBr (11)	328	4.5×10^3	330	320
PhCF (12)	270	1.9×10^4	††	320

* In a 3-methylpentane glass at 77 K.

† In isooctane solution at room temperature.

§ Wavelength of maximum absorption, data in parentheses are for other prominent maxima.

‖ The minimum extinction coefficients for each band (see text).

¶ Wavelength of maximum absorption determined using the transient absorption apparatus using a bandpass of 4 nm, with analysis every 2 or 4 nanometers.

** Wavelength at which the time-resolved kinetic data were determined.

†† This value could not be determined due to absorption by the diazirine starting material.

yet, it is not known whether these discrepancies reflect a small extent of side reaction of the carbenes which does not lead to cyclopropane, or whether the differences are a consequence of a more complex kinetic scheme (vide infra). The absolute kinetic results evidently support the vast steady-state relative rate literature, and thus the conclusions drawn therefrom.[1,2]

The current technique does not, however, allow direct access to the absolute reactivity of all carbenes, because as previously indicated, detection of the carbene relies on optical absorption in an easily accessible part of the spectrum. For this reason, only carbenes with aryl groups on the carbene center have as yet been studied. Additional requirements are that only the carbene precursor, and not the quencher, should absorb light appreciably at the excitation wavelength, and that neither should absorb appreciably at the analyzing wavelength.

Absolute rate constants for carbene reactions

For quenching of each of the carbenes by the simple olefins, it is observed that the rate constants decrease in the order 3 > 5 > 6 > 7, i.e. they decrease regularly with decreasing olefinic alkylation. Plots of log (k_{abs}) for carbenes 2a–e versus olefin ionization potentials of the substrates yield similar slopes (-2.1 to -2.6 eV^{-1}), but the relatively poor correlation coefficients (0.971 to 0.985) indicate that other factors could also influence the rate constants for the addition reactions. The alkene substituent effect is in accord with the well-known features of carbene/alkene additions.[1–3a, 14] Additionally the results are consistent with the proposal that the addition of electrophilic carbenes to alkenes is dominated by interaction of the vacant carbene p orbital with the π electrons of the olefin.[14] In this case, increasing electron donating ability of the olefin would be expected to stabilize such an interaction.

The experiments on the *para*-substituted carbenes provide direct evidence concerning the electronic distribution within the transition state (Table 3). It is observed that electron withdrawing groups in the position *para* to the carbene center increase the rate constants for reactions with all of the olefins. Hammett plots of the data for the five carbenes are linear for each olefin (Fig. 10). It is found that σ_p^+ values yield the best fit to the data.[15] Remarkably the four correlations are almost parallel and yield moderately positive ρ values of 1.5, 1.4, 1.5 and 1.6 for alkenes 3, 5, 6 and 7. Two properties of the substituents may influence the reactivity of the carbene. Electron donating groups can stabilize carbenes by means of π type resonance interactions and thus carbene 2b should be less stable than 2e. Electron withdrawing groups should favor the
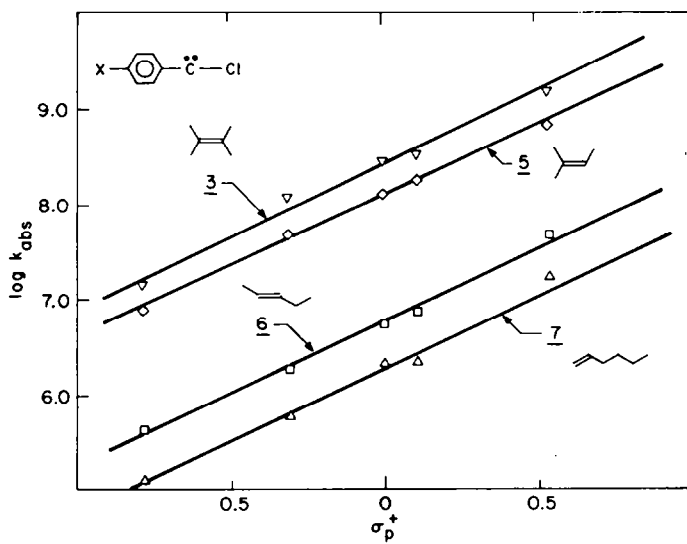
Fig. 10. Plots of log (k_{abs}) versus σ_p^+ for the reaction of carbenes 2a–e with olefins 3 and 5–7 in isooctane.

carbene/alkene transition state due to stabilization of the enhanced negative charge there imposed on the carbenic carbon.[14a] The positive ρ values indicate that either effect may be important, although the temperature dependencies of these reactions suggest that entropic rather than enthalpic factors may be more important (*vide infra*).

The dependence of the selectivity of the five carbenes on their *para*-substituents is surprising. The spread in rate constants from the fastest (**2b** + **3**) to the slowest (**2e** + **7**) reaction is four orders of magnitude, but the spread in rate constants over the four alkenes is almost the same for each carbene (Table 3). This behavior apparently does not conform to the usual rule that selectivity and reactivity are related. This effect possibly implies a multistep reaction mechanism (*vide infra*).

Hammett plots for quenching of the four carbenes **2a-e** with the four styrenes are given in Fig. 11. In these cases, the correlations are appreciably nonlinear. For carbene **2c** a fairly good straight line is obtained with a ρ value of -0.9. This result is in agreement with the experiments of Dürr who found ρ values of -1.06 to -0.58, depending upon the temperature, for the reaction of **2a** with **8a-d**, from steady-state competition experiments.[16] However, curvature in the Hammett plots was not observed in these experiments, and the correlations for **2a** (X = H) were linear. The negative values of ρ for these reactions are consistent with the conclusions drawn from the study of the effect of *para*-substitution on the carbene because ρ values with opposite signs are obtained for the carbene and the quencher. However, as the carbenes become more electron rich distinct upward curvature in the plots is observed. For the most electron deficient carbene (**2b**) a downward curve is observed. The data are consistent

with a change in the character of the addition from electrophilic to nucleophilic as the substituents on the carbene and alkene are altered appropriately.

Thus for the electron rich carbene **2e**, we observe a larger rate constant for addition to styrene **8a** than to **8c** (Table 4). If the plots were continued to large positive values of σ_p^+ then a cross-over of the five lines would occur as the nucleophilic character became more important. This is the first apparent case of ambiphilic carbenic reactivity as investigated by absolute rate measurements. The apparent ambiphilicity of these phenylchlorocarbenes in additions to styrenes is surprising indeed. The *bona-fide* ambiphiles methoxychlorocarbene[17] and phenoxychlorocarbene[18] are known to be ambiphilic toward styrenes, but the new observations for carbenes **2a** and **2d-e** warrant further study and evaluation.

The rate constant data given in Table 5 illustrate the effect of substitution at the carbene center. In these cases the selectivities of the three carbenes (PhCF > PhCCl > PhCBr) follow the expected order based upon their respective reactivities. The most reactive carbene (**11**) is also the least selective, and the least reactive carbene (**12**) is the most selective. The order of "spreads" in the rate constants is identical to the order of the m values for these carbenes determined from steady-state competition experiments. Thus, in this case, the data provide a clear example of a normal reactivity-selectivity relationship. The reactivity order Br > Cl > F can be explained in terms of the relative stabilities of the carbenes.[14a,19] These stabilities depend both upon lone pair donation by the carbenic halogen substituent to the vacant carbenic p orbital, which will be greatest for X = F and least for X = Br,[14a] and the extent to which the electronegativity of the halogen causes an increase in p character in the σ orbital.[19]

Stabilization (if any) of a phenylchlorocarbene by *para*-substitution of the phenyl ring (carbenes **2a-e**) presumably occurs by π type resonance interaction of the carbenic p orbital with the phenyl ring. This will be influenced by the electronic nature of the substituent. The different degrees of stabilization for the phenylhalocarbenes (PhCX vs ArCCl) may manifest themselves in the relative reactivities observed with the two sets of carbenes.

The extent and ordering of stabilization of the carbenes may be qualitatively estimated from their electronic spectra. The HOMOs of the arylhalocarbenes are most certainly π orbitals associated with the aryl ring, whereas the LUMOs of the singlet carbenes will be the unoccupied p orbitals.[14a] It is probable that the largest effect of the adjacent halo group on the carbenes **11** and **12** is on the LUMO and not on the ring HOMO. Assuming that the observed absorptions (Figs 8 and 9, Table 7) are due to π-p transitions then we observe that the p LUMO increases in energy (the wavelength of the transition decreases) in the order Br < Cl < F. This is consistent with a corresponding increase in electron donating ability of the substituent.[19]

According to perturbation theory, the optimum situation for the carbene alkene transition state interaction is one in which the carbene LUMO and alkene HOMO are closest in energy.[14a] As the energy of the carbene LUMO increases (PhCF > PhCCl > PhCBr), the energy gap with a given alkene increases and the rate constant decreases. Thus the reactivity
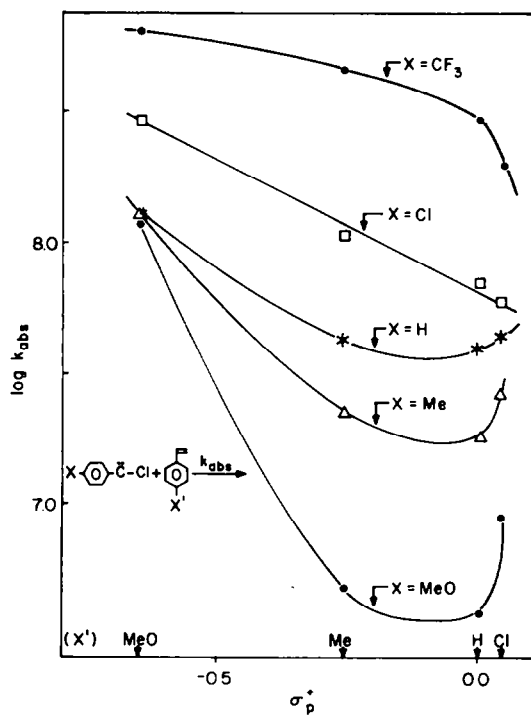

Fig. 11. Plots of log (k_{abs}) versus σ_p^+ for reaction of styrenes **8a-d** with carbenes **2a-e** in isooctane.

differences observed (Table 5) for the phenylhalocarbenes are consistent with the corresponding differences in their LUMO energies, as observed in their electronic spectra. The same relationship is not observed so clearly for the carbenes 2a–e, presumably because in these cases the substituents strongly affect the π ring (HOMO) orbitals as well as the carbene LUMO.

Temperature effects

The results of these experiments can be summarized as follows: (1) the plots for the fastest reactions ($k_{abs} > 10^8$) show pronounced curvature, and negative activation energies are observed at higher temperatures; (2) the plots for the slower reactions show either small negative or small positive activation energies ($E_a < 2$ kcal mol^{-1}) with the slowest reactions having the largest values of E_a. The activation energies for all of the reactions studied are less than the expected value for diffusion. The data may be interpreted in terms of a kinetic model in which a reversibly formed carbene/alkene complex is an intermediate in the reaction as shown in eqns (2) and (3), in which C, A and C/A represent the carbene, alkene and complex re-

$$C + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C/A \qquad (2)$$

$$C/A \overset{k_2}{\longrightarrow} \text{cyclopropane} \qquad (3)$$

spectively (Fig. 13). For this mechanism the carbene decay will obey first order kinetics if the steady-state approximation is valid for C/A, i.e. if

$$k_1 \ll (k_{-1} + k_2) \qquad (4a)$$

$$[C][A]k_1 = (k_{-1} + k_2)[C/A]. \qquad (4b)$$

In this case the observed quenching constant (k_{abs}) is given by

$$k_{abs} = k_1 k_2/(k_{-1} + k_2). \qquad (5)$$

Therefore the slope of a plot of the first order decay constant for the carbene versus quencher concentration is linear (as observed) and the steady-state

relative rate constant determination should agree with those from the absolute rate experiments.[20] However this may not be true if eqn (4) is not valid, i.e. the complex has a non-negligible lifetime.[20] For the condition $k_2 \ll k_{-1}$, in which dissociation to starting materials is faster than formation of product, then

$$k_{abs} = (k_1/k_{-1})k_2 \qquad (6)$$

in which (k_1/k_{-1}) is the equilibrium constant (K_{eq}) for complex formation. If we assume that k_1 represents diffusion controlled formation of the complex then we may determine the quantity (k_{-1}/k_2) using the expression

$$(k_{-1}/k_2) = (k_{diff} - k_{abs})/k_{abs}. \qquad (7)$$

The value of k_{diff} as a function of temperature can be estimated from a simplified form of the Debye equation.[21]

$$k_{diff} = 2 \times 10^5 \, T/\eta \qquad (8)$$

Thus the quantity (k_{-1}/k_2) can be determined as a function of temperature. Appropriate data for the reactions of phenylchlorocarbene with the alkenes 3 and 5–7 plotted against $(1/T)$, are shown in Fig. 12. The result of this manipulation is to transform the Arrhenius data of Fig. 4 into a set of four straight lines. Indeed, we find that all of the curved Arrhenius plots for all of the reactions we have studied become straight lines upon this operation. From the plots of (k_{-1}/k_2) versus $1/T$, values of $\Delta\Delta G^*$, $\Delta\Delta H^*$ and $\Delta\Delta S^*$ can be computed for the competition between the dissociation of the complex and the completion of cycloaddition (Fig. 13) using eqns (9) and (10). These values are summarized in Table 8 for all of the reactions studied.

$$\ln (k_{-1}/k_2) = \Delta\Delta G^*/RT \qquad (9a)$$

$$\Delta\Delta G^* = \Delta G_2^* - \Delta G_1^* \qquad (9b)$$

$$\ln (k_{-1}/k_2) = 1/R(\Delta\Delta H^*/T - \Delta\Delta S^*). \qquad (10)$$

The data in Table 8 show that in each case the enthalpy requirement for product formation is smaller than that for dissociation for the complex. However, the entropy
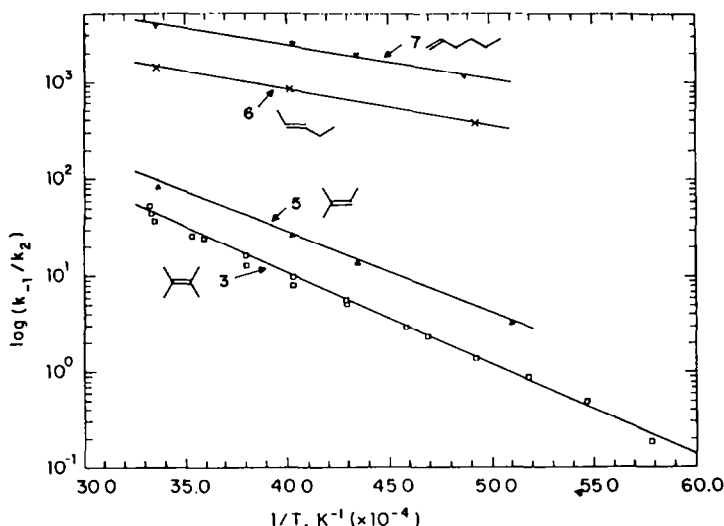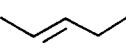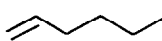

Fig. 12. Plots of log (k_{-1}/k_2) versus $(1/T)$ for the reaction of phenylchlorocarbene with alkenes 3 and 5–7 in isooctane.

Table 8. Calculated differential activation parameters for cyclopropanation versus dissociation for the carbene/alkene complex

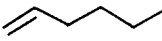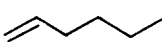| Alkene	Carbene	Solvent	k_{abs}*	$\Delta\Delta H^*$†	$\Delta\Delta S^*$†	$\Delta\Delta G^*$§
(tetramethylethylene)	PhCCl	isooctane	2.2×10^8	−4.4	−23	2.2
(trimethylethylene)	PhCCl	isooctane	1.3×10^8	−3.7	−22	2.7
(2-pentene)	PhCCl	isooctane	5.5×10^6	−1.6	−20	4.5
(1-hexene)	PhCCl	isooctane	2.2×10^6	−1.5	−21	5.1
(tetramethylethylene)	p-CF$_3$PhCCl	isooctane	1.5×10^9	−4.2	−23	1.1
(tetramethylethylene)	p-MeOPhCCl	isooctane	1.4×10^7	−2.6	−22	4.0
(tetramethylethylene)	PhCCl	toluene	1.4×10^8	−3.4	−20	2.6
(tetramethylethylene)	PhCCl	acetonitrile	1.1×10^8	−1.6	−15	2.8
(tetramethylethylene)	PhCBr	isooctane	3.8×10^8	−4.7	−22	2.0
(tetramethylethylene)	PhCF	isooctane	1.6×10^8	−4.4	−24	2.5
(1-hexene)	PhCBr	isooctane	4.0×10^6	−1.4	−21	4.7
(1-hexene)	PhCF	isooctane	9.3×10^5	−1.2	−23	5.6

* Rate constants at room temperature ($l\ mol^{-1}\ s^{-1}$).
† Derived from plots of $\log (k_{-1}/k_2)$ versus $1/T$ (see text). Units are $kcal\ mol^{-1}$ or $cal\ mol^{-1}\ deg^{-1}$.
§ Derived directly from eqn (9) (see text). Units are $kcal\ mol^{-1}$.

restrictions for cyclopropanation are much greater than for dissociation; typically values of $\Delta\Delta S^*$ of ca −20 e.u. are found. However the differential activation entropies are similar for each olefin addition and small differences cannot be distinguished from experimental error. Consequently, although .the reactions are essentially entropy controlled (their temperature dependencies are small), it is the differences in their enthalpy requirements which govern the values of $\Delta\Delta G^*$, and therefore the rate constants for reaction. Thus, for the reactions of 2a with olefins 3 and 5–7, we observe a decrease in the differential activation enthalpies with increasing substitution of the alkene. This is consistent with the increased electron donating ability of the alkene and increased stabilization of the transition state for cyclopropane formation. Similarly, examining the reactions of carbenes 2a, b, e with alkene 3, the electron donating methoxy substituent destabilizes the transition state with respect to dissociation, consistent with the importance of charge-transfer character in the transition state.

However, halogen substitution at the carbene center does not have as clear an effect. Thus, the differential activation enthalpies for reactions of 2a, 11 and 12 with 3 or 7 are similar for each carbene for either olefin. The
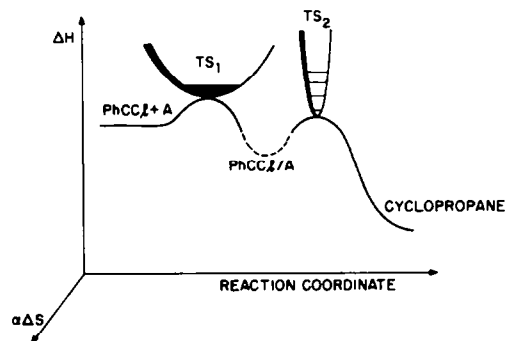

Fig. 13. Possible potential surface for the reaction of a singlet carbene with an alkene showing the intermediacy of a complex.

small changes in rate constants for these systems, although in appropriate order, cannot be definitively attributed to changes in $\Delta\Delta H^*$ or $\Delta\Delta S^*$ with certainty. These observations support a conclusion that substituent variation on the carbene's phenyl ring, or substitution at the alkenic carbon atoms affect the stabilization of the addition reaction transition state to a larger extent than halogen variation at the carbene center.

Finally we observe a significant change in $\Delta\Delta S^*$ for reaction of **2a** with **3** in acetonitrile as compared to isooctane (or toluene). However we also note a complimentary change in $\Delta\Delta H^*$ so that the overall reaction rate is slower. It is not known whether this compensation is real or if the separation of enthalpy and entropy is suspect in this case.

The nature of the complex

There exists in the literature a number of examples of "negative" activation energies in solution phase organic reactions. These include the quenching of fluorescent excited states,[22] quenching of triplet benzophenone by alkenes,[23] reaction of singlet oxygen with a variety of substrates,[24] reaction of nitryl ylides with electron deficient olefins[25] and a Diels–Alder reaction.[26] In each case, the kinetic data have been interpreted in terms of reversible complex formation. However, the structure of the intermediate complex is not revealed by the kinetic analysis. In the present case, a structure which is consistent with current ideas concerning the reactions of singlet carbenes with alkenes is that of a loose charge-transfer complex, in which there is interaction between the vacant p orbital of the carbene and the π electrons of the alkene. The question remains whether the intermediate is truly a complex or simply a proximity or contact pair in a solvent cage.[27] In the latter situation it is possible for $\Delta\Delta H^*$ to be negative if the enthalpy required for product formation is less than the activation energy for diffusive separation of the contact pair. However, it is unlikely that there will be no binding between the vacant carbenic p orbital and the alkene π electrons within a carbene/alkene contact pair.

In this respect the recent results of Houk et al. are of interest.[28] Using an *ab initio* technique these workers have found that for certain systems, interaction of the carbene and alkene is sufficiently strong so that there is no enthalpic barrier to product formation, and that no potential energy minimum exists for a complex. If this were the case for the phenylchlorocarbene addition to tetramethylethylene then the only barrier to cyclopropane formation would be entropic. Under these conditions a negative temperature coefficient for the reaction rate may be observed if, as T is lowered, the free energy barrier to product formation (dominated by $T\Delta S^*$) decreases faster than RT.[29] Under these considerations the enthalpic barrier TS_2 in Fig. 13 would be zero, but the relative entropic barriers TS_1 and TS_2 would remain. As the temperature decreases it becomes less difficult to pass the narrow TS_2 barrier to product formation, whereas the wide diffusive separation barrier is relatively unaffected. Thus the probability of product formation for each carbene/alkene encounter would increase with decreasing temperature. A negative temperature coefficient would also occur if the enthalpic barrier to product formation were smaller than that for dissociation

because at lower temperatures the complex would be more likely to take the lowest energy pathway out of the free energy well (Fig. 13). Indeed, for the less substituted alkenes, the enthalpic barrier does become more significant as shown by their increasing differential activation enthalpies (Table 8). It is probable that the actual situation is somewhere between the two examples given here for the structure of the complex. We envisage diffusion controlled formation of a solvent cage encounter pair which is partially stabilized by weak charge-transfer interactions, and lies in a free energy well defined on one side by the activation energy for diffusive separation and the weak binding energy, and on the other side by small enthalpic and high entropic barriers to product formation. The binding energy for the intermediate complex must be weak because this species must have a sufficiently short lifetime so that the approximation of eqn (4) holds.

The intermediacy of a short-lived complex is compatible with the absolute kinetic analysis of the structure/reactivity relationships for the carbenic systems described previously. The relative rate constants determined from the steady-state and the time-resolved experiments should agree if the complex is short-lived. A Hammett relationship for the kinetic situation described by eqn (6) is valid and a linear plot should be observed,[20b] except that the slope of such a plot will be given by

$$\text{slope} = \rho(\text{eq}) + \rho(2) \qquad (11)$$

in which $\rho(\text{eq})$ and $\rho(2)$ are the ρ values associated with the equilibrium for the carbene and olefin with the complex, and the formation of the cyclopropane respectively. Thus the determined ρ value represents a maximum value for the cyclopropanation reaction because the ρ value for the equilibrium will be zero for simple diffusion in and out of a solvent cage, and positive if any significant binding occurs within the complex.

For the kinetic situation described by eqn (5) a Hammett plot need not be linear unless the complex is a simple diffusion controlled encounter species which does not show any Hammett dependence, or unless each of the relevant rate constants are affected similarly by the substituents. As in the previous case either situation is likely, thus the Hammett plots for each reaction in which the mechanism does not change are linear (Fig. 10). In each case, the ρ values are a true reflection of the extent to which the *para*-substituents affect the reactivity of the carbenes. The data shown in Fig. 11 are consistent with a change in reaction mechanism (transition state character) with changing substitution of the olefin quencher.

The reactivity-selectivity principle (RSP)[3b,c] has played an important role in the interpretation of carbene relative rate data. It is thus surprising that for the reactions of **2a–e** with the simple alkenes we observe no RSP (Table 3). Several examples of non-RSP behavior have been observed in other reaction systems,[30] and indeed RSP has recently been severely criticized.[30b] Often the mechanisms of reactions which do not show RSP involve more than one process in the rate determining step,[30] as in eqns (2) and (3). However this does not explain why RSP is observed (Table 5) for the reactions of the halocarbenes **2a, 11** and **12**, although only a small rate range is covered in this case. In this regard it is of interest to note that RSP is

observed for the reactions of halocarbynes with simple alkenes.[31] The usefulness of RSP as applied to carbene reactions has been demonstrated on many occasions, but our data suggest that the relationship should not be relied on exclusively for *a priori* predictions of carbenic reactivity or selectivity.

CONCLUSIONS

The determination of the absolute reactivities of the carbenes described above clearly indicate that much valuable information can be obtained using these newer methods of investigation. It is of great importance to emphasize that the absolute rate data do not in any way discount earlier conclusions based upon the results of traditional steady-state relative rate experiments. However, the experiments described here have allowed a very detailed examination of the origins of carbenic reactivity and selectivity which only became possible using the time-resolved technique. For example the results of the variable temperature absolute rate studies suggest the existence of transient carbene/alkene intermediates which were not previously implicated. Additionally, we have been able to obtain direct information about the relative ordering of the vacant p orbitals of the singlet arylhalocarbenes by means of their absorption spectra. We are certain that time-resolved techniques will continue to provide valuable new information about the basic chemistry of carbenes and other transient species in organic chemistry.[24,25]

EXPERIMENTAL

All of the alkene quenchers were distilled immediately prior to use and spectrograde solvents were used in all cases. The transient absorption apparatus consisted of a 300 watt Xenon arc lamp (Varian Eimac), ISA H-10 monochrometer and RCA 4840 photomultiplier tube as the monitoring system. Samples were photolyzed in 1 cm^2 cuvettes. The PMT output was terminated using a 50 ohm load resistor and analyzed using a Tektronix 7912 AD transient digitizer as part of a Tektronix WP2252 signal processing system. The laser used was a Lambda Physik Excimer Laser EMG-101 which emits *ca* 100 mJ of light at 351 nm in *ca* 15 ns.

The diazirines were prepared according to previously described procedures,[9,11,32] except for phenylfluorodiazirine which was prepared from phenylbromodiazirine by exchange with fluoride ion.[33]

The relative rate measurements were carried out according to the standard method.[1b,3a] Appropriate cross-checks were performed.

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