Activation Parameters for the Additions of Arylhalocarbenes to Alkenes

Robert A. Moss,*1 Witold Jawornyicz,2 Nicholas J. Turro,*1 Ian R. Gould,1 and Yuan Cha2

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and the Department of Chemistry, Columbia University, New York, New York 10027. Received May 6, 1986

Abstract: By use of nanosecond laser flash photolytic methods, absolute rate constants have been obtained for the additions of p-(trifluoromethyl)phenylbromocarbene (CF3C6H4CBr), phenylbromocarbene (PhCBr), phenylchlorocarbene (PhCCl), phenylfluorocarbene (PhCF), and p-methoxyphenylfluorocarbene (CH3O C6H4CF) to tetramethylethylene (TME) and 1-hexene. The rate constants ranged from 1.7 \cdot 10^{10} \text{L/(M.s)} \text{ for} (CF3C6H4CBr/TME) \text{ to} 5.0 \cdot 10^{10} \text{L/(M.s)} \text{ for} (CH3O C6H4CF/1-hexene); classical structure/reactivity relations were obeyed. Determination of the rate constants at temperatures between 315 and 200 K gave \( E_a, \log A, \Delta H^*, \Delta S^*, \) and \( \Delta G^* \) for the 10 reactions. All of the reactions were dominated by \( \Delta S^* \). \( \Delta G^* \) ranged from 5.0 to 11 kcal/mol for the fastest and slowest reactions. Negative values of \( E_a \) were observed for some of the faster reactions at higher temperatures. These results are analyzed in terms of single-step addition reactions where \( \Delta G^* \) is dominated by \( \Delta S^* \) and, alternatively, in terms of a two-step mechanism proceeding through a carbene/alkene complex.

Nearly 20 years ago, Skell and Cholod used variable-temperature relative rate measurements to dissect the contributions of differential activation entropies and enthalpies in the additions of CCl3 to alkenes.1 Although \( \Delta G^* \) varied with alkene structure in an understandable way, it was the entropic term, rather than the enthalpic term, that usually paralleled the rates and was the dominant contributor to \( \Delta G^* \); only with the less reactive 1-alkenes did enthalpy dominate. Application of the Hammond postulate led to suggestions that more reactive carbenes and alkenes reacted via later, tighter, enthalpy-controlled transition states.*s2

More recently, the experiments of Giese3 and the theoretical studies of Houk4 have strongly emphasized the role of entropy in carbene/alkene addition reactions. The applicability of nanosecond laser flash photolysis to the determination of absolute rate constants for (singlet) aryhalocarbenes/alkene addition reactions5 allows us an opportunity to directly examine Skell’s suggestions,1 as well as certain of Houk’s predictions.4

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Additions of Arylhalocarbenes to Alkenes

Table I. Absolute Rate Constants for Carbene/Alkene Additions

<table>
<thead>
<tr>
<th>carbene</th>
<th>TME</th>
<th>1-hexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CF3C6H4CBr</td>
<td>1.7 ± 0.05 x 10^10</td>
<td>2.4 ± 0.1 x 10^10</td>
</tr>
<tr>
<td>PhCBr</td>
<td>3.8 ± 0.3 x 10^10</td>
<td>4.0 ± 0.4 x 10^10</td>
</tr>
<tr>
<td>PhCCI</td>
<td>2.8 ± 0.2 x 10^10</td>
<td>2.2 ± 0.2 x 10^10</td>
</tr>
<tr>
<td>PhCF</td>
<td>1.6 ± 0.2 x 10^10</td>
<td>9.3 ± 0.5 x 10^10</td>
</tr>
<tr>
<td>p-CH3OC6H4CF</td>
<td>1.1 ± 0.04 x 10^10</td>
<td>5.0 ± 0.3 x 10^10</td>
</tr>
</tbody>
</table>

*Rate constants were measured at 23-25 °C. Units are M⁻¹ s⁻¹.*

In the absence of alkene quenching experiments (see below). In the absence of alkene, the carbene decayed by pseudo-first-order reaction with an unknown quencher; its lifetime was ~20 µs at 25 °C.

To determine the absolute rate constants for the alkene additions, diazirine solutions in spectrograde isooctane were diluted of the carbene spectra was pseudo first order and linearly dependent on the quencher concentration. A plot of the rate constant *k_ads* decreases of ~14- and 19-fold with TME and 1-hexene substrates, respectively. Conversely, p-trifluoromethyl substitution on phenylbromocarbene engenders _normal_ reactivity/selectivity behavior.*

In order to obtain activation parameters for these reactions, we determined the absolute rate constants at various temperatures between ~315 and 200 K. With the TME substrate, all of the carbenes except _p_-CH3OC6H4CF gave _curved_ Arrhenius plots of the type that we encountered previously.* As we reproduce the temperature dependence of _k_ads_ for the _p_-CF3C6H4CBr/TME reaction in Figure 1. These Arrhenius relations led to negative _E_a_’s at higher temperatures (~310-263 K) and small (0.2-1.3 kcal/mol) "normal" _E_a_’s at lower temperatures. With _p_-CH3OC6H4CF/TME and 1-hexene (for all carbene substrates), normal Arrhenius behavior was observed. The activation parameters, _E_a_ and log _A_, are collected in Table II.

We estimate the errors in the activation parameters to be ±0.5 kcal/mol in _E_a_ and ±0.5 unit in log _A_ (Table II).

Similarly clear is the effect of alkene structure, where TME > hexene > PhCBr: PhCF > PhCCI > PhCBr > p-CH3OC6H4CF, in accord with classical ideas about carbene structure/stability/reactivity relationships.* Similarly clear is the effect of alkene structure, where TME > 1-hexene by ~70 with _p_-CF3C6H4CBr and ~220 with _p_-CH3OC6H4CF. Note, too, that the less reactive 1-hexene "spreads" the rate constants of the five carbens over a wider range (480) than does the more reactive TME (154). These observations comprise normal reactivity/selectivity behavior.*

Steady-State Photolytic Studies. Simple cyclopropane adducts of PhCBr, PhCBr, and PhCF have been long known and well characterized. More importantly, they are obtainable by photolysis in alkenes of the diazirines 2-4.* In the present study, the cyclopropane adducts of the new carbens (_p_-CH3OC6H4CF and _p_-CF3C6H4CBr) with TME and 1-hexene were isolated from steady-state photolyses (> 300 nm) of diazirines 1 and 5 in these alkenes. The products were purified by chromatography (SiO2/pentane) and characterized by NMR and exact mass spectroscopy or elemental analysis. As a check on the absolute kinetic data (Table I), we determined the product-based, relative rate constants, _k_ads/k REF_, by the standard alkene competition method.* The relative rate constants were 185 for _p_-CH3OC6H4CF and 69.3 for _p_-CF3C6H4CBr, which agree reasonably well (within experimental error) with the corresponding ratios of the absolute rate constants (220 and 70, respectively) from Table I.

Discussion

Structure/Reactivity Dependence. The substitution of the p-methoxy substituent on phenylfluorocarbene is seen from Table I to be worth _k_ads_ decreases of ~14- and 19-fold with TME and 1-hexene substrates, respectively. Conversely, p-trifluoromethyl substitution on phenylbromocarbene engenders _normal_ reactivity/selectivity behavior.*

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can obtain. The solvent is isooctane, and the reference temperature is 298 K. See text for a discussion of the derivation and meaning of these values. This entry is slightly less accurate due to a slight curvature in the plot of (log (k1/k2)) vs. 1/T.

encountered in the higher temperature regime for the more reactive carbene/alkene combinations (cf. Table I and Figure 1). These alternative treatments are key to two different mechanistic models for the carbene/alkene addition reaction. In the model of Houk et al.,24 the carbene adds to the olefin in a single step, no intermediates intervene, and the activation free energy is dominated by a large, positive $-\Delta S^*$ term that increases sharply as the carbene approaches the olefin. In this model, $\Delta H^*$ decreases (i.e., is negative) as the reaction proceeds for such reactive carbenes as CBr2. Noting that $\Delta H^* = E_1 - R T$, this is the case that corresponds to those reactions with $E_1 < 0$ in Table I. It is entropic, engendered by the reaction energy surface, that is responsible for the activation barrier in the Houk carbene addition model.24 A second way of interpreting the data is to postulate that a reversibly formed carbene/alkene complex is an intermediate in the reaction; cf. eq 1 and 2. Here, C is the carbene, A is the alkene, and C/A is the complex. This scheme has previously been used to interpret other examples of carbene additions with negative activation energies,9a and it is related to analogous mechanisms for other examples of fast bimolecular reactions.5e We have shown9e that the mechanism of eq 1 and 2 gives rise to eq 3, where $k_{2}/k_{1} = (k_{2} \text{- diffusion})/k_{2} \text{- bond}$.

In contrast to the behavior of log $k_{2}/k_{1}$ with temperature, plots of log $(k_{1}/k_{2})$ vs. 1/T are linear,24 and from their slopes one can obtain differential activation parameters, e.g., $\Delta S^*$, in which the $\Delta S^*$ represents the value for $k_1$ (complex cyclorpanation) less the value for $k_2$ (complex dissociation). The results of applying this model to the temperature-dependent kinetic data for the reactions of Table I are shown in Table III.

We can also convert15 the Arrhenius data of Table II into absolute values of $\Delta H^*$, $\Delta S^*$, and $\Delta G^*$ suitable for discussion of the Houk reaction model. This is done in Table IV. It is conceivable that diffusion control becomes significant or dominant with the fast reactions at lower temperatures (<250 K), leading to curvature of the $k_{2}/k_{1}$ (T) correlations, positive values of $E_1$ and $\Delta H^*$, and "subversion" of the entropic control manifested at higher temperatures (320–260 K). Put another way, solvent viscosity and diffusion may generate the "stickiness" necessary for the intervention of carbene/alkene complexes in the low-temperature regions. These considerations lead us to include only the high-temperature data for the first three TME reactions in Table IV.

Comparison of Reaction Models. We cannot yet distinguish between entropic control of carbene additions by the reaction energy surface16 or carbene/alkene reversible complexation16 in these reactions. Each model has particular advantages in analysis of the experimental data.

The carbene complex mechanism has become very popular as an aid to the rationalization of complex kinetic data for competitive carbene reactions.16 However, carbene/alkene complexes have yet to be directly observed, and we cannot take kinetic fitting as conclusive evidence for their existence. Indeed, the kinetic data can often be explained in ways that do not involve a carbene/alkene complex.17 In sum, the principal advantages of the carbene complex model are that it leads naturally to a rationalization of the negative activation energies often observed in carbene/alkene additions and that it has precedent in mechanisms applied to other reactive intermediates.24 On the other hand, it complicates an understanding of the vast body of relative rate data for carbene additions obtained by classical alkene competition reactions.11 The complication is not fatal, however, and mechanistically useful structure/reactivity correlations can be made in terms of the complex model (see below and ref 5b, 5c, and 5e).

There are also advantages to the Houk model,4 which is better suited to discussions of either the transition-state parameters of Table IV or Skell's predictions.1 This model also allows discussion of the classical relative rate data18 in straightforward terms without the necessity of invoking the intermediacy of a complex. In the remainder of this Discussion section, we will briefly analyze the temperature-dependent kinetic data according to each of the reaction models. Our concern will be to highlight, wherever we can, common ground shared by the two mechanistic models.

In terms of the Houk model, we focus on the observation that comparisons of $-\Delta S^*$ with $\Delta G^*$ (Table IV) show that all of these reactions are entropy controlled;16 even in the "slow" p-CH3OC6H5CF/1-hexene reaction, $-\Delta S^*$ is 78% of $\Delta G^*$. This general entropic control and $\Delta H^* > 0$ observed for the TME additions (as well as p-CH3OC6H5CF/1-hexene) are consonant with Skell's findings for CCl1 and Houk's analysis for the alkene additions of "reactive" carbones such as CBr2 or p-CH3OC6H5CF.20

### Table III. Differential Activation Parameters for Carbene Reactions

<table>
<thead>
<tr>
<th>Carbene</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$\Delta G^*$</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$\Delta G^*$</th>
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<tbody>
<tr>
<td>p-CF3C6H4CF/1-hexene</td>
<td>2.2</td>
<td>21</td>
<td>7.5</td>
<td>2.2</td>
<td>21</td>
<td>7.5</td>
</tr>
<tr>
<td>PhBr</td>
<td>-4.4</td>
<td>-23</td>
<td>2.2</td>
<td>-1.5</td>
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<td>5.1</td>
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<tr>
<td>PhCCI</td>
<td>-4.4</td>
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<td>2.2</td>
<td>-1.5</td>
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<td>PhCF</td>
<td>-4.4</td>
<td>-23</td>
<td>2.2</td>
<td>-1.5</td>
<td>21</td>
<td>5.1</td>
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<td>p-CH3OC6H5CF/1-hexene</td>
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<td>2.2</td>
<td>21</td>
<td>7.5</td>
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### Table IV. Activation Parameters for Carbene/Alkene Additions

<table>
<thead>
<tr>
<th>Carbene</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$-\Delta S^*$</th>
<th>$\Delta G^*$</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$-\Delta S^*$</th>
<th>$\Delta G^*$</th>
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<tbody>
<tr>
<td>p-CF3C6H5CF/1-hexene</td>
<td>-1.6</td>
<td>22.6</td>
<td>6.5</td>
<td>-0.19</td>
<td>25</td>
<td>7.4</td>
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<tr>
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<td>p-CH3OC6H5CF</td>
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<td>-29</td>
<td>8.6</td>
<td>9.3</td>
<td></td>
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</tbody>
</table>

(14) Riddick, J. A.; Burger, W. Tech. Chem. (N. Y.) 1970, 2, 95. We used the relation $k_{2}/k_{1} = 2 \times 10^{27}/T$ between $k_{2}/k_{1}$, temperature, and viscosity. Note that the approximation of $k_{1}/k_{2}$ may be poorer in the least reactive systems such as p-CH3OC6H5CF/1-hexene. However, the differential activation parameters that result (Table III) appear reasonable.


(19) This conclusion is common to the carbene complex model as well; see below.

(20) Our data show p-CH3OC6H5CF to be a good "model" for CBr2, so that entropic control is anticipated. Houk et al.23 have given a good model for the "stabilized"17 CBr2 enthalpic dominance predicted17 for this species is not realized with p-CH3OC6H5CF. From the latter's probable structure/reactivity correlations can be made in terms of the complex model.
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kabs has not yet been measured for a carbene as stabilized as CF3, and we can now appreciate that this order of stability is unreachable in the arylihalocarbenes series, where even p-CH3OC6H4CF is only comparable with CCI3. Therefore, we cannot yet provide a total demonstration of Skell's predictions,1 which would require a reactivity spectrum broad enough to encompass the transition from ΔS3 to ΔH* control. As one moves from the most to the least reactive carbene/alkene pair of Table III, allowing for the imprecision of kab, and we can now appreciate that this order of stability is unreachable.

kabs consists of p-CF3C6H4Br with TME, where it is a test of these predictions for FCOMe may soon be possible. We note that these extrapolations and predictions should be independent of the model chosen to discuss the data.

Application of the carbene complex model to the kinetic data generates the differential activation parameters that appear in Table III. Again, we observe that the entropy terms are dominant; therefore, as we found earlier, the differential entropies of activation are, with the exception just noted, all very similar. Therefore, in any comparison of the reactivities of alkene pairs, relative rate constants (i.e., rate constant ratios) will depend upon the differences in ΔH* that ultimately appear in ΔG*

That is, with ΔS3 nearly constant, the relative enthalpies for cyclopropanation, a barrier arising primarily in the loss of the principal component of ΔG*, for any selected reaction, is entropic. Nevertheless, as we found earlier, the differential entropies of activation are, with the exception just noted, all very similar. Therefore, in any comparison of the reactivities of alkene pairs, relative rate constants (i.e., rate constant ratios) will depend upon the differences in ΔH* that ultimately appear in ΔG*.

We have termed this effect "the de facto enthalpic control," and its practical expression is the larger kabs values observed for cyclopropanations of the more highly substituted alkienes; e.g., TME > 1-hexene, in accord with the classical structure/reactivity analysis of the carbene/alkene addition reaction.10 Thus, although ΔS3* is usually the same for reactions of ArCX with either TME or 1-hexene (Table III), ΔH* is always more favorable (i.e., more negative) for the TME reaction. This means that ΔH* for the cyclopropanation, from the complex, is enthalpically better than dissociation of the complex, to a greater extent, when the alkene is TME than when it is 1-hexene. This is consistent with the increased electron-donating ability of the more highly substituted alkene and the resultant increased stabilization of the transition state for cyclopropanation formation.

We close by noting that the Houk and carbene complex models for addition will approach each other as the carbene increases in stability. For a stabilized, relatively unreactive carbene, ΔG* should be dominated by enthalpy. The energy surface for the alkene addition of this species will resemble those commonly encountered for other cycloadditions (e.g., the Diels–Alder reaction), and both ΔH* (or E2) and ΔS3* will be of appropriate sign and magnitude. However, in such a "well-behaved" carbene/ alkene addition, cyclopropanation will be attended by a large activation barrier that will dwarf the barrier into or out of any prior carbene/alkene complex. Accordingly, the formation or dissociation of such a complex will be kinetically unimportant in either reactivity or selectivity considerations.

It is only when a carbene is highly reactive, and the activation barrier to cyclopropanation is very low, that a weakly bound carbene/alkene complex, perhaps best regarded as an encounter pair in a solvent cage, can play any role in the kinetics. This is also the setting where, in the absence of a size-able enthalpic barrier to cyclopropanation, a barrier arising primarily in the loss of translational entropy can dominate the overall reactivity.4

Experimental Section

Diazirines. The carbene precursors, diazirines 1–5, have been fully characterized, and preparative details have been furnished.21

Cyclopropanes. Adducts of PhCBr, PhCCl, and PhCF to TME and 1-hexene were obtained by photolysis (λ > 300 nm) of diazirines 2–4 in these alkenes as described in the literature.22 The new adducts of p-CH3OC6H4CF and p-CF3C6H4Br to TME and 1-hexene were prepared similarly, according to the following procedure illustrated for the adduct of p-CF3C6H4CF and 1-hexene.

Diazirine 5 (0.30 g, 1:mmol) was mixed with 0.72 g (8.6 mmol) of 1-hexene and photolyzed for 5 h in a Pyrex tube with the light from a 200-W, focused Osram XE mercury lamp. The reaction temperature was maintained at 25 °C by a water bath, and the reaction mixture was stirred magnetically. Excess hexene was removed by simple distillation, and the residual oil was purified by chromatography on silica gel with pentane elution. We thus obtained 23.6 mg (0.074 mmol, 7%) of pure adduct, characterized, and preparative details have been furnished.*q9


(22) That ΔS3* in keeping with Houk's representation of ΔS* for carbene/alkene additions as a single, reactant-independent function of reactant separation, the largest component of which is due to the decrease in translational entropy. In terms of the carbene complex model, Houk's ΔS* would correspond to ΔS3* for cyclopropanation from the complex. However, ΔS3* for complex formation of cyclopropanation reaction is governed by a wide and "ineffective" path3* which should also be reactant independent. Therefore, ΔS3* would be nearly constant, regardless of carbene and alkene identity.

(23) This adduct was a mixture of syn and anti isomers that were separable by capillary GC (see note 25 for conditions). The isomer distributions were 1.0–1.2 with p-CF3C6H4Br and 1.0–1.3 with p-CH3OC6H4CF.

About 1 Hr of long-range HF coupling was visible in both pairs of methyl groups.

(25) Quantitative GC analyses employed a Varian Model 3700 instrument interfaced to a Varian Model 4270 electron integrator. All separations were carried out with a 12-m, 0.22-mm (internal diameter) Varian bonded-phase, vitreous silica BP 1 (equivalent to SE-30) column, operated at 170 °C. Injector and detector temperatures were 230 °C and 300 °C, respectively, and N2 carrier gas was supplied at 14 psi. The flame ionization detector was calibrated with pure adducts.

(24) About 1 Hz of long-range HF coupling was visible in both pairs of methyl groups.

(25) Quantitative GC analyses employed a Varian Model 3700 instrument interfaced to a Varian Model 4270 electron integrator. All separations were carried out with a 12-m, 0.22-mm (internal diameter) Varian bonded-phase, vitreous silica BP 1 (equivalent to SE-30) column, operated at 170 °C.
Electronic Structure of Cyclic Bicalicenes

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Abstract: The novel π-electron system, pentacyclo[11.0.0.02,4.03,5.011,3,9,7,11,13,15-octane ("cyclic bicalicene") has been prepared, in which two calicene units are joined in a head-to-tail manner. The X-ray crystallographic analysis indicates that the cyclic bicalicene skeleton is completely planar; i.e., the molecule has $D_{3h}$ symmetry. Cyclic bicalicene is shown to have a characteristic absorption band at around 500 nm, which is interpreted as an intramolecular charge-transfer band by a SCF–CI MO method. From the $^1$H NMR spectra, the paramagnetic ring current due to peripheral 16π conjugation is not observed. The $^1$H and $^13$C NMR chemical shifts suggest that a considerably large polarization of each calicene unit occurs in the cyclic system. The alternating polarization in cyclic bicalicene is also supported by the graph-theoretical and SCF MO calculations.

Cyclopropenylidene cyclopentadienide (calicene) (1) is a cross-conjugated π system, whose synthesis and characterization have been of keen interest. Thus far, the parent calicene has not been isolated. However, a number of calicene derivatives substituted with strong electron-donating and/or electron-withdrawing groups at the cyclopropenyl and/or cyclopentadienyl rings have been isolated as stable compounds. From the investigation of their electronic character, it has been shown that a polar structure (1B) contributes significantly to the ground state.

Recently, we have succeeded in the isolation of the 3,11-bis-(tert-butylthio) derivative 2a as a stable crystalline compound. This compound contrasts in stability to 5,6-bis(tert-butylthio)-calicene, which is unstable even at -78 °C and which evidences "aromatic" system with a 16π-electron periphery, we have investigated its electronic structure and π-conjugation mode based on $^1$H and $^13$C NMR spectral data. X-ray structural analysis, and graph-theoretical and a modified Pariser–Parr–Pople-type SCF MO methods ("the variable integrals method") and elucidated the cause of stabilization. In addition, acyclic bicalicene has been synthesized as a reference π system for cyclic bicalicene. Since the electronic spectrum of cyclic bicalicene is very characteristic, the character of electronic transition is interpreted by using the

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(1A) (1B)

(2a): X=SBu
(2b): X=H
(2c): X=SnBu

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