SHORT COMMUNICATION

ABSOLUTE RATE CONSTANTS FOR THE REACTIONS OF PHENYLHALOCARBENES WITH ALKYNES

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Additions of phenylchlorocarbene and phenylfluorocarbene to representative alkynes are rapid (10^6–10^7 l mol^{-1} s^{-1}). The variation of the rate constants with alkyne structure parallels that observed with analogous alkene substrates. The addition of phenylchlorocarbene to 3-hexyne is characterized by a very low activation energy (~ 2 kcal mol^{-1}) and a large, negative entropy of activation (~ -20 e.u.).

INTRODUCTION

Despite extensive studies of the absolute kinetics of carbene additions to alkenes,[1] there appears to have been no survey of carbene/alkyne kinetics. Additions of carbenes to alkynes lead to cyclopropenes and cyclopropenium ions,[2] important classes of small-ring compounds. The absence of kinetic characterization here constitutes a lacuna in our knowledge. We have now addressed this deficiency with a laser flash photolysis (LFP) study of the absolute kinetics of reactions of phenylchlorocarbene (PhCCl) and phenylfluorocarbene (PhCF) with representative alkynes. The measured rate constants were compared with those obtained previously for analogous carbene/alkene reactions.

RESULTS

Kinetics

PhCCl and PhCF were generated by LFP[3] of pentane or isooctane solutions of phenylchlorodiazirine (1a)[4] or phenylfluorodiazirine (1b),[5] and reacted with 3-hexyne (2), phenylacetylene (3), ethoxyacetylene (4), 1-heptyne (5), methyl propiolate (6) or dimethyl acetylenedicarboxylate (7). Thus, diazirine 1a or 1b was irradiated at 22 °C with a 14-ns, 70–90 mJ, 351-nm pulse from an XeF excimer laser,[3] affording the known[1e] transient UV absorptions of PhCCl or PhCF. These absorptions, monitored at 315 nm (PhCCl) or

1a, X=Cl
1b, X=F

2 $C_2H_5-C{\equiv}C-C_2H_5$

$R-C{\equiv}C-H$ $CH_3COO-C{\equiv}C-OOCCH_3$
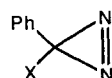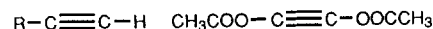
3, R=Ph   **7**
4, R=C_2H_5O
5, R=n-C_5H_{11}
6, R=CH_3COO

310 nm (PhCF), were quenched on addition of alkynes 2–7 and, in the presence of sufficiently high concentrations of alkyne (0·01–1·5 M, depending on the alkyne reactivity), the transients decayed with pseudo-first-order kinetics. The slopes of the linear correlations of the decay rate constants vs [alkyne] then afforded bimolecular rate constants, k_2, for the carbene/alkyne reactions. These are collected in Table 1. Table 2 gives absolute rate constants for reactions of these carbenes with alkenes that are structurally analogous to alkynes 2–7. Literature values for substrate ionization potentials are included in each table.

Comparisons of the rate constants in Tables 1 and 2 reveals substantial correspondence between the kinetic behavior of PhCCl or PhCF with alkynes 2–7 or with the analogous alkenes. Both the magnitudes of k_2

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Table 1. Absolute rate constants for reactions of PhCX and alkynes[a]

Alkyne	IP (eV)[b]	$10^{-6} k_2$ (l mol^{-1} s^{-1}) PhCCl	$10^{-6} k_2$ (l mol^{-1} s^{-1}) PhCF
PhC≡CH	8·82[c]	22	11
C_2H_5C≡CC_2H_5	9·32[d]	24	8·4
C_2H_5OC≡CH	9·5[e]	6·8	[f]
$C_5H_{11}C$≡CH	10·4[d]	4·3	1·6
CH_3OOCC≡CH	11·2[e]	1·8	1·1
CH_3OOCC≡$CCOOCH_3$	11·5[g]	5·3	3·2

[a] At 22 °C in isooctane; estimated error, ±10%.
[b] Ionization potential.
[c] Ref. 6.
[d] Ref. 7.
[e] Ref. 8.
[f] Not determined; an unknown growth signal occurred after LFP, and interfered with PhCF signal decay.
[g] Ref. 9.

Table 2. Absolute rate constants for additions of PhCX to alkenes[a]

Alkene	IP (eV)[b]	$10^{-6} k_2$ (l mol^{-1} s^{-1}) PhCCl	$10^{-6} k_2$ (l mol^{-1} s^{-1}) PhCF
$PhCH$=CH_2	8·48[c]	40[d]	—
trans-CH_3CH=CHC_2H_5	9·04[e]	5·5[d]	2·4
n-C_4H_9OCH=CH_2	9·14[f]	4·7[f]	—
n-C_4H_9CH=CH_2	9·48[e]	2·2[d]	0·93[d]
CH_3OOCCH=CH_2	10·72[c]	5·1[g]	1·4[g]
trans-C_2H_5OOCCH=$CHCOOC_2H_5$	11·23[h]	3·3[f] 9·2[i]	—

[a] At 22–25 °C in isooctane; estimated error, ±10%.
[b] Ionization potential.
[c] Ref. 6.
[d] Ref. 1e.
[e] Ref. 10.
[f] Ref. 1d; k_2 determined in toluene.
[g] Ref. 11.
[h] Ref. 9.
[i] Ref. 1d (heptane).

(10^6–10^7 l mol^{-1} s^{-1}) and the selectivity patterns of the carbenes are similar. With the alkynes, in addition to the alkenes, we observe decreasing carbenic reactivity with increasing substrate π ionization potential, i.e. electrophilic carbenic selectivity, until the substrate's ionization potential increases to ≥11 eV. Then, with strongly electron-deficient substrates, k_2 *increases* as the known,[1d,12] latent nucleophilicity of the phenylhalocarbenes comes into play. The carbene additions to 7 clearly seem to be predominantly nucleophilic, consistent with the behavior anticipated from simple differential frontier molecular orbital energy considerations.[1c]

Not only are the rate constants of the carbene/alkyne and carbene/alkene reactions similar, but, in the case of 3-hexyne, the activation parameters are also comparable. Thus, an Arrhenius treatment of ln k_2 vs $1/T$ (250 ≤ T ≤ 308 K) for the addition of PhCCl to alkyne 2 gives $E_a = 2·1 ± 0·1$ kcal mol^{-1} (1 kcal = 4·184 kJ) and log $A = 8·93 ± 0·08$ s^{-1}, with a correlation coefficient of 0·996 (see Figure 1). These parameters are similar to those obtained for the addition of PhCCl to trans-pent-2-ene: $E_a = 1·0$ kcal mol^{-1} and log $A = 7·7$ s^{-1}.[13] In both
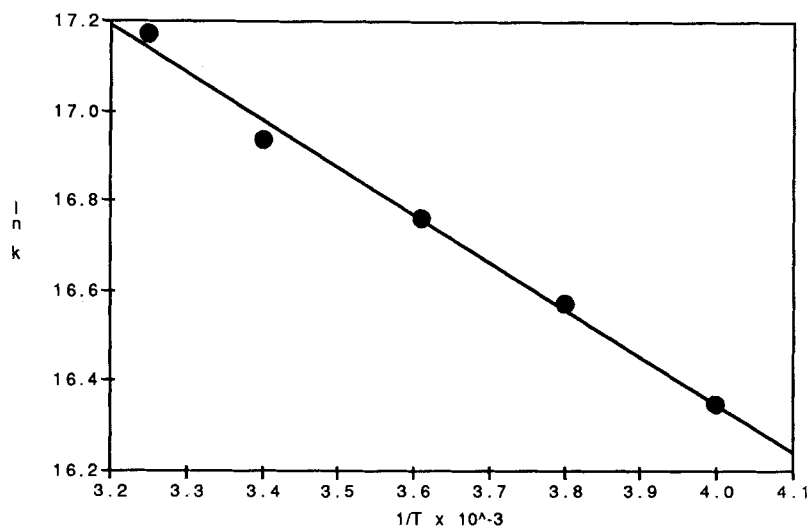
Figure 1. ln k_2 (l mol^{-1} s^{-1}) vs $1/T$ (K^{-1}) for the addition of PhCCl to 3-hexyne (2)

reactions, the activation parameters are dominated by abnormally low pre-exponential factors, i.e. large, negative activation entropies,[13,14] -19.5 e.u. for the PhCCl 3-hexyne addition and -25.0 e.u. for the PhCCl/trans-pent-2-ene reaction. Entropic control of bimolecular kinetics, a now commonplace observation for the highly exothermic reactions of carbenes and alkenes,[1a] clearly also extends to alkyne substrates.

Products

The products of PhCX additions to 3-hexyne were fully characterized. Thus, UV photolysis ($\lambda > 330$ nm) of phenylhalodiazirines in a 5–10-fold excess of 2 gave yellow solids 8a-c, after removal of hexyne. The crude yields were 8a (from PhCF) 15%, 8b (from PhCCl) 23% and 8c (from PhCBr[4]) 47%. All three products exhibited identical, appropriate NMR spectra in D_2O (sodium 2,2-dimethyl-2-silapentane-5-sulphonate (DSS)) with the Et groups at $\delta 1.40$ (t, $J = 4$ Hz, CH_3) and 3.23 (q, $J = 7.4$ Hz, CH_2), and aromatic resonances at $\delta 7.59$ (t, $J = 7.5$ Hz, 2H, m), 7.78 (t, $J = 7.4$ Hz, 1 H, p) and 8.04 (d, $J = 7$ Hz, 2H, o). The chloride salt, 8b, was converted to tetrafluoroborate 8d with $AgBF_4$ in acetonitrile. We obtained 8d as a white solid, m.p. 100–101 °C, in 83% yield. Its NMR spectrum was identical with that of 8b, and a satisfactory elemental analysis (C, H, F) was obtained.

8a, X=F
8b, X=Cl
8c, X=Br
8d, X=BF₄

9

10

11
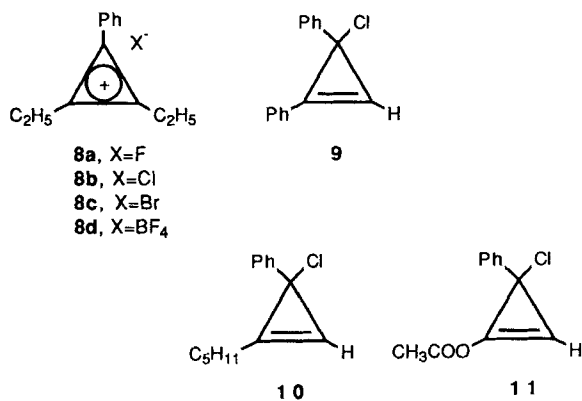
Cyclopropenes that are *monosubstituted* at C=C, particularly when the single vinyl substituent is electron withdrawing, are generally unstable and difficult to isolate.[15] This applies to the adducts of PhCX to 6.[15] The adduct of PhCCl to phenylacetylene has been prepared by thermolysis of 1a with 3 in refluxing benzene; product cyclopropene 9 was characterized, but was unstable when impure.[16]

We briefly examined the photolyses of 1a in 1-heptyne (5) and methyl propiolate (6). The former reaction, in pentane, gave a brown oil that exhibited an appropriate NMR spectrum for cyclopropene 10. In particular, the pentyl group appeared at (δ, CDCl₃)

0.95 (t, Me), 1.44 (m, CH_2CH_2) 1.85 (t, CH_2) and 2.74 (t, allylic CH_2). The vinyl H was observed as a singlet at $\delta 4.83$; the corresponding resonance in 9 appeared at $\delta 4.95$.[16] Attempts to purify 10 by chromatography on silica gel led to decomposition. The crude yellow oil resulting from the photolysis of 1a in 6 had NMR signals consistent with expectations for 11, including a vinyl proton singlet at δ(CDCl₃) 4.8. As anticipated,[15] however, 11 decomposed on attempted chromatography.

CONCLUSION

The addition reactions of PhCCl and PhCF with representative alkynes are rapid (10^6–10^7 l mol^{-1} s^{-1}) processes, with rate constant and selectivity dependences on alkyne structure that are comparable to those observed with analogous alkenes. The addition of PhCCl to 3-hexyne is dominated by entropy ($\Delta S^{\ddagger} = -20$ e.u.), and exhibits a low activation energy ($E_a \approx 2$ kcal mol^{-1}). The kinetic selectivity patterns of the carbenes toward the alkynes are generally electrophilic, but with very electron-deficient alkynes (e.g. dimethyl acetylenedicarboxylate), the latent nucleophilicity of these ambiphilic carbenes is manifested.

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