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Study of Chlorine Atom Abstraction Reactions of Phenylchlorocarbene by Laser Flash Photolysis

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We have previously reported the absolute rate constants of Cl atom abstraction by triplet diphenylcarbene and dibenzocycloheptadienylidene.[1] The interpretation of the data was complicated by issues of intersystem crossing and singlet/triplet surface crossings. This prompted the present study of Cl abstraction by a singlet carbene uncomplicated by considerations of carbene spin multiplicity. We chose to study phenylchlorocarbene (**1**) because this carbene is a ground-state singlet and is conveniently generated from the corresponding diazirine. Carbene **1** has been extensively studied by *l*aser *f*lash *p*hotolysis (LFP)[2] although its reaction with chlorine donors has not been previously considered. In fact, reactions of phenylchlorocarbene with olefins have been studied in CCl_4 as solvent.[3] This study illustrates potential mechanistic hazards with the use of this material as a phenylchlorocarbene reaction solvent.

Photolysis of 3-phenyl-3-chlorodiazirine (**2**) in CCl_4 gives a mixture of products consistent with the occurrence of some chlorine atom abstraction/radical recombination in addition to products formed by reaction of **1** with itself and with diazirine precursor.[4] The observation of a clean mixture of radical coupling products **4**–**6** is unsurprising after the fact because CIDNP studies have revealed that both singlet and triplet methylene can abstract chlorine from chloroform and carbon tetrachloride.[5]

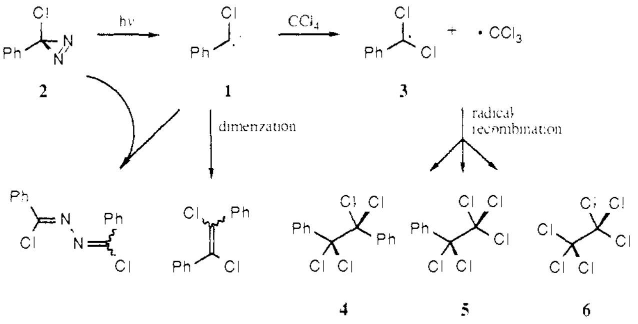
The absolute bimolecular rate constants of reaction of phenylchlorocarbene (**1**) with chlorine donors are listed in Table I. The rate constants were obtained by LFP of diazirine **2** in the presence of variable amounts of chlorine donating quencher. It was more convenient to monitor the effect of the quencher using pyridinium ylide **7**[6] rather than observing the absorbance of **1** itself, as a probe of the carbene kinetics, due to spectral overlap between phenylchlorocarbene **1** (λ_{max} = 318 nm)[2] and dichlorobenzyl radical **3** (λ_{max} = 324 nm).[7] The absolute rate constants could be obtained by monitoring the effect of quencher on the rate of formation of **7** or on the yield (top OD) of the ylide. The two methods gave consistent results. For example k(**1** + CCl_3CN, toluene), direct = $1.43 \pm 0.16 \times 10^7$ M^{-1} s^{-1} and = 1.47×10^7 M^{-1} s^{-1} by Stern–Volmer analysis of the ylide top OD.[6] In the case of k(**1** + $CCl_2(CN)_2$, toluene), direct = $8.45 \pm 0.71 \times 10^9$ M^{-1} s^{-1}, and Stern–Volmer analysis gives 8.11×10^9 M^{-1} s^{-1}.

Table I. Absolute Rate Constants for Chlorine Atom Abstraction by Phenylhalocarbenes

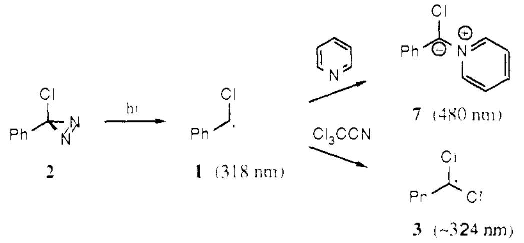
carbene	Cl donor	solvent	k (M^{-1} s^{-1})
1	CCl_4[a]	acetonitrile	$3.8 \pm 1.6 \times 10^4$
1	CCl_3CN	toluene	$1.4 \pm 0.2 \times 10^7$
1	$CCl_2(CN)_2$	toluene	$8.4 \pm 1.4 \times 10^8$
1	CCl_3CN	acetonitrile	$4.0 \pm 1.0 \times 10^8$
9	CCl_3CN	toluene	$1.1 \pm 0.2 \times 10^8$

[a] This rate constant is probably an upper limit. The small size of this rate constant leads to imprecision due to incompletely suppressed second-order processes. We are also able to estimate this from competition data on DEM/CCl_4 mixtures.

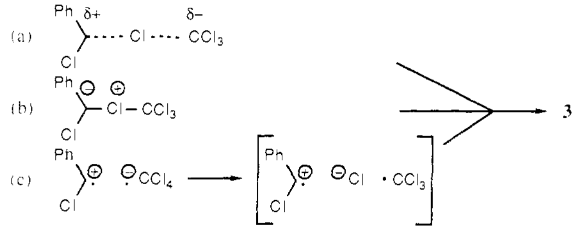
Scheme I



Scheme II



Chlorine transfer can proceed via (a) simple but polar atom transfer, (b) formation of a chloronium ylide[8] which subsequently fragments, or (c) dissociative electron transfer followed by ion pair collapse. The polarities in mechanisms (a) and (c) are similar and opposite to that of (b) which allows their differentiation. Successive replacement of Cl by CN on the chlorine donor would be expected to destabilize ylide **8** and retard the rate. Cyano substitution actually greatly increases the rate constant which is more consistent with mechanisms (a) and (c). Further evidence for these polar types of mechanisms come from the observation that p-methoxyphenylchlorocarbene (**9**)[2] reacts 10 times faster with CCl_3CN than does parent carbene **1** in toluene. Finally we note that if (b) were operative we would expect to detect ylide **8** by analogy to our other ylide work involving phenylchlorocarbene.[6,9] In conclusion the evidence does not support the intervention of a chloronium ylide[8] in the reaction of phenylchlorocarbene with the halomethanes. The generality of this conclusion to other carbene–halogen systems is open to question. Experiments are in progress to distinguish pathways (a) and (c).



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