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First Direct Observation of Reactive Carbenes in the Cavities of Cation-Exchanged Y Zeolites

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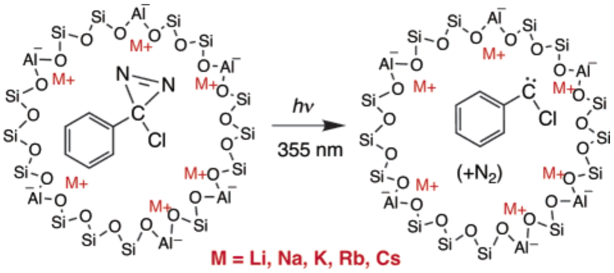
ABSTRACT



Herein we report the first direct observation of reactive carbenes within the cavities of cation-exchanged Y zeolites. Chloro(phenyl)- and bromo(phenyl)carbenes were generated upon laser photolysis of 3-halo-3-phenyldiazirines incorporated within dry zeolites and the absolute reactivity of the carbenes was investigated as a function of counterbalancing cation and coincorporated quenchers in order to elucidate the behavior of these intermediates within zeolites. Product analysis performed upon thermolysis of the diazirine in Y zeolites yielded products that were identified as those derived from the carbene.

Zeolites are microporous crystalline aluminosilicate materials made up of corner-linked $[SiO_4]^{-4}$ and $[AlO_4]^{-5}$ tetrahedra, where every aluminum present in the framework carries a net negative charge that must be balanced with a charge-balancing cation.[1,2] The arrangement of the tetrahedra units results in an open framework structure consisting of cavities and pores where organic guest molecules can be readily incorporated. The negative network of well-defined void spaces and associated counterbalancing cations generates a polar matrix with localized electrostatic fields and active acidic and basic sites. As a result, there has been considerable interest in the ability of these supramolecular materials to modify and/or promote a variety of fundamental reactions in organic chemistry.[3−11] From these studies the reactivity and decay pathways of several different types of reactive species have been investigated within these heterogeneous solid supports.

However, little has been reported regarding the behavior of reactive carbenes within the motion-restricted media of zeolites.[12,13] Carbenes are neutral compounds that present a divalent carbon, which is linked to two adjacent groups by covalent bonds, and two nonbonding orbitals containing, between them, two electrons. To date, no time-resolved studies of reactive carbenes within zeolites have been reported. The direct detection and study of reactive carbenes within the cavities of zeolites will give important information

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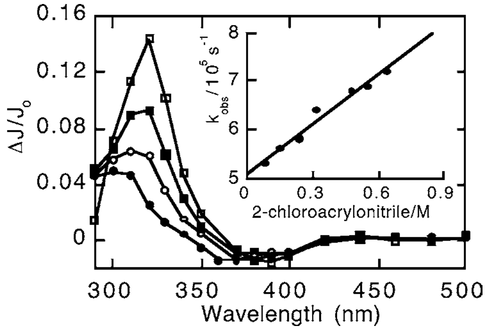


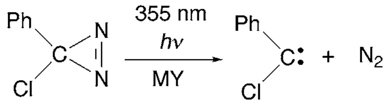
Figure 1. Transient diffuse reflectance spectrum generated (□) 1.52, (■) 2.68, (○) 4.24, and (●) 13.0 μs after 355 nm laser irradiation of 3-chloro-3-phenyldiazirine in dry RbY under vacuum (10^{-4} Torr) conditions. Insert shows the observed rate constant for the decay of the 320 nm band as a function of increasing 2-chloroacrylonitrile concentration.

about the behavior of this reactive intermediate within the intrazeolite environment.

In the present work, we describe results concerning the generation and reactivity of chloro(phenyl)- and bromo(phenyl)carbenes within cation-exchanged Y faujasites using nanosecond diffuse reflectance spectroscopy. These results constitute the first direct observation of carbenes within zeolites.

The transient diffuse reflectance spectrum generated upon 355-nm laser flash photolysis (Nd:YAG laser, ≤ 10 mJ, <8 ns/pulse) of 3-chloro-3-phenyldiazirine[14] ($PhClCN_2$) incorporated into dry RbY (loading level of $\langle s \rangle = 0.1$ molecules of $PhClCN_2$ per zeolite supercage) under vacuum conditions (10^{-4} Torr) is dominated by an intense absorption band centered at 320 nm, Figure 1. The 320 nm transient decays in a first-order fashion with an observed rate constant of $k_{obs} = 3.6 \times 10^5$ s^{-1}. At long time scales after the 320 nm band has completely decayed the spectrum is dominated by a long-lived absorption band centered at 300 nm.

The position and narrow shape of the absorption band at 320 nm closely resembles that of chloro(phenyl)carbene (PhClC:) previously observed in solution.[15] In addition, the transient observed at 320 nm is not affected by the introduction of oxygen into the zeolite but is rapidly quenched in the presence of typical carbene quenchers such as methanol ($k_{MeOH} = 2.1 \times 10^5$ M^{-1} s^{-1}) and 2-chloroacrylonitrile, 2-CAN ($k_{2-CAN} = 3.4 \times 10^5$ M^{-1} s^{-1}), Figure 1. These observations are similar to those typically observed for singlet halo(aryl)carbenes in solution[15] and lead to the conclusion that the transient species at 320 nm is the chloro(phenyl)carbene formed within the zeolite upon laser photolysis of $PhClCN_2$, eq 1 (X = Cl). In agreement with this identification is the weak bleaching (i.e., loss of absorbance) in the 350−400 nm region of the spectrum, which is due to the photodecomposition of the diazirine precursor upon laser excitation.

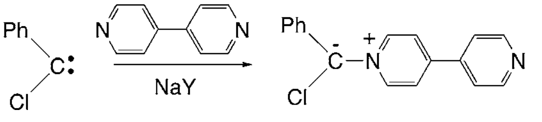


1a, X = Cl
1b, X = Br
2a, X = Cl
2b, X = Br

(1)

The same transient species with an absorption maximum at 320 nm as well as bleaching between 350 and 400 nm is observed upon laser photolysis of $PhClCN_2$ incorporated within the cavities of dry CsY under vacuum (10^{-4} Torr) conditions. In KY, bleaching along with a small absorption band at 320 nm due to the carbene is also evident, but the spectrum is now dominated by the long-lived 300 nm band. In LiY and NaY, bleaching in the 350−400 nm region is still seen, but no absorption due to the carbene at 320 nm could be observed. Since the photochemical quantum yield of the diazirine precursor is not expected to be highly dependent on the nature of the counterbalancing cation, the similar bleaching observed in the zeolites suggests that a similar amount of carbene is generated in all cases. Thus, the absence of carbene absorption in NaY and LiY suggests that the carbene is too short-lived to be directly observed using the nanosecond laser technique, whereas in KY only a small fraction of the photogenerated carbenes are sufficiently long-lived to be observed. For the transient diffuse reflectance spectra of $PhClCN_2$ in the five cation-exchanged zeolites, see Supporting Information.

To provide further evidence that the carbene is generated in NaY, experiments were carried out using 4,4′-bipyridine to trap the carbene and generate a long-lived ylide.[16] Pyridine is more commonly used to generate such ylides, but it binds strongly to the zeolite framework, thus reducing its ability to trap the carbene.[17−19] 4,4′-Bipyridine will also bind to the framework, but its second reactive nitrogen will remain free for addition to the carbene. Figure 2 shows the transient diffuse reflectance spectrum generated after 355 nm laser irradiation of 3-chloro-3-phenyldiazirine co-incorporated in NaY with 4,4′-bipyridine under dry vacuum conditions. The transient spectrum is dominated by a large broad band centered at 550 nm. The location of the absorption maximum at 550 nm and the broad shape of the band coincide nicely with the absorption spectrum of the PhClC:-4,4′-bipyridyl ylide in solution[20] and is formed upon a fast reaction between the co-incorporated 4,4′-bipyridine with the photogenerated carbene, eq 2.



(2)

Ylide formation in NaY, where the carbene is too reactive to be directly observed, provides strong additional evidence

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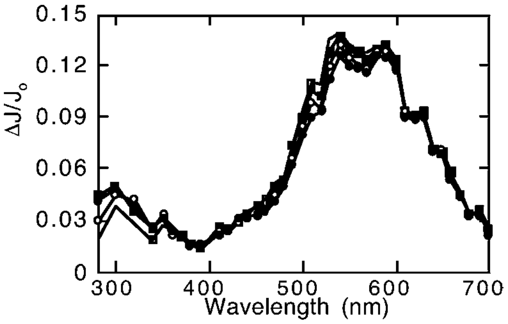

Figure 2. Transient diffuse reflectance spectrum generated (□) 1.44, (■) 3.92, (○) 8.48, and (●) 14.3 μs after 355 nm laser irradiation of 3-chloro-3-phenyldiazirine (⟨s⟩ = 0.1) and 4,4′-bipyridine (⟨s⟩ = 2) co-incorporated in NaY under dry vacuum conditions (10^{-4} Torr).

for the formation of the carbene within this supramolecular host and also indicates that the reactive carbene can be trapped within the cavities of the zeolite.

Thermolysis at 70−80 °C for 24 h of zeolite samples of NaY and CsY incorporated with $PhClCN_2$ under dry nitrogen conditions leads to the formation of benzaldehyde and 2,5-diphenyl-1,3,4-oxadiazole as the major products, Table 1.

Table 1. Relative Product Yields Obtained upon Thermolysis at 70−80 °C of 3-Chloro-3-phenyldiazirine Incorporated in Dry Y Zeolites under Nitrogen

zeolite	$PhClCN_2$ occupancy level (⟨s⟩)	benzaldehyde (%)	2,5-diphenyl-1,3,4-oxadiazole (%)
NaY	0.5	94	3
NaY	2	43	57
CsY	0.5	88	12

The formation of benzaldehyde and 2,5-diphenyl-1,3,4-oxadiazole can be reasonably explained through carbene decay pathways. The formation of benzaldehyde may be rationalized by a mechanism involving O−H insertion of PhClC: into intrazeolite water, followed by loss of HCl.[21] 2,5-Diphenyl-1,3,4-oxadiazole can be produced from the reaction between PhClC: and the diazirine, $PhClCN_2$. This reaction initially gives bis(α-chlorobenzylidine)hydrazine,[22−24] which reacts further with intrazeolite water over the lengthy reaction time to give the observed product.[25]

The significant increase in the product yield for the oxadiazole from 3% to 57% as the loading level of the diazirine increases from ⟨s⟩ = 0.5 to ⟨s⟩ = 2 is consistent with this product being generated by reaction of the carbene with its precursor, Table 1.

Results from laser experiments with 3-bromo-3-phenyldiazirine[26] ($PhBrCN_2$) incorporated within KY and RbY under vacuum conditions are closely similar to those obtained for $PhClCN_2$ in RbY and CsY. Laser irradiation of $PhBrCN_2$ incorporated within these cation-exchanged zeolites (⟨s⟩ = 0.1) yields transient diffuse reflectance spectra dominated by a strong absorption band centered at 340 nm that decays on the microsecond time scale. Weak bleaching in the 370−410 nm region is observed, indicating the consumption of the diazirine precursor upon laser excitation. The 340 nm absorption maximum and the shape of the absorption band closely match those of the bromo(phenyl)carbene (PhBrC:) previously reported in solution.[27] In addition, the introduction of oxygen has no influence on the decay rate constant or absorption characteristics of the transient spectra. Furthermore, vapor inclusion of methanol or 2-CAN rapidly quenches the intensity of the signal at 340 nm and increases the observed rate constant for the decay of the transient. All of these observations allow the absorption band observed at 340 nm generated upon irradiation of the $PhBrCN_2$ in dry KY and RbY under vacuum conditions (10^{-4} Torr) to be confidently assigned to PhBrC:, eq 1 (X = Br).

In CsY laser photolysis of $PhBrCN_2$ under vacuum conditions leads to a transient absorption spectrum that shows a small decaying absorption band centered at 340 nm. The reduced intensity of the band at 340 nm in CsY indicates that in this cation-exchanged zeolite most of the photogenerated carbenes are too reactive to be observed on the nanosecond time scale. PhBrC: was not directly detected in either LiY or NaY, presumably because the carbene is too short-lived in these zeolites. For the transient diffuse reflectance spectra of $PhBrCN_2$ in the five cation-exchanged zeolites, see Supporting Information.

The observed first-order rate constants for the decay of the halo(phenyl)carbenes in the Y zeolites are presented in Table 2. In each zeolite where the carbenes could be observed, both carbenes are quite short-lived and decay with rate constants similar to those observed for the same carbenes in hydrocarbon solvents.[15] Thus, the zeolite cavity does not provide an environment with the ability to substantially increase the lifetime of the carbenes. The rate constants for the decay of chloro(phenyl)carbene in Table 2 also reveal a general trend whereby the rate constant for the decay of the carbene in the different alkali-metal exchanged zeolites decreases as the size of the cation increases. This trend is difficult to rationalize if, as suggested by the product studies, the main reactions causing the rapid decay of the carbenes involve addition to water and the precursor diazirine. In both

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(20) In hexane solution chloro(phenyl)carbene reacts rapidly with 4,4′-bipyridine to form the PhClC:-4,4′-bipyridyl ylide which, typical of carbene ylides, has a broad band with an absorption maximum at 510−520 nm. The decay of the carbene at 320 nm and the growth of the ylide at 520 nm increase in a linear fashion upon increasing concentration of 4,4′-bipyridine leading to a bimolecular rate constant of 2.0×10^9 M^{-1} s^{-1}.

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Table 2. Absolute First-Order Rate Constants (k_{obs}) for Decay of Halo(phenyl)carbenes in Dry Alkali Metal Cation Exchanged Y Zeolites under Vacuum (10^{-4} Torr) Conditions

	k_{obs} (10^5 s^{-1})	
zeolite	chloro(phenyl)carbene	bromo(phenyl)carbene
LiY	not observed	not observed
NaY	not observed	not observed
KY	5.2 ± 0.5	4.5 ± 0.4
RbY	3.6 ± 0.4	2.5 ± 0.2
CsY	3.1 ± 0.3	4.9 ± 0.5

cases, the quenchers should be more strongly bound to the framework in the small cation zeolites and therefore less available for reaction. Thus, the carbene would actually be less reactive as the size of the alkali-metal cation decreases, a trend observed previously in the quenching of carbocations with quenchers such as methanol.[28] Furthermore, the amount of both quenchers in the zeolites is small ($<$1 wt % of water) and presumably cannot account for the rapid quenching of the carbene in NaY and LiY. In addition, changing the loading level of the diazirine precursor between $\langle s \rangle = 0.5$ and 0.05 had no influence on the decay rate constant of the PhClC: in RbY. Only at very high loading levels of diazirine ($\langle s \rangle > 1$) does the observed rate constant increase slightly with increasing loading level, which is consistent with the coupling reaction occurring at high loading levels.

Instead, the decrease in the rate constants parallels the electron-accepting ability, or Lewis acidity, of the zeolites upon going from LiY to CsY.[29,30] This leads to the suggestion that the main reaction responsible for the time-resolved disappearance of the carbene involves an interaction of the carbene with Lewis acid sites within the zeolites cavities. This interaction is likely to be sufficiently weak for the carbene to eventually be displaced from the framework by water or the diazirine as these quenchers migrate into a cavity possessing a carbene-framework complex. Future investigations are ongoing to provide more insight into the decay pathway of reactive carbenes in cation-exchanged Y zeolites in order to elucidate further mechanistic details for these interesting reactions.

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Supporting Information Available: Time-resolved diffuse reflectance spectra generated upon photolysis of 3-chloro-3-phenyldiazirine and 3-bromo-3-phenyldiazirine in cation-exchanged Y zeolites, methods used for sample preparation, and a brief description of the nanosecond laser system. This material is available free of charge via the Internet at http://pubs.acs.org.

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