

recognition techniques can be of use in the classification of drugs as to their pharmacological activity.

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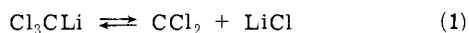
Matrix Reactions of Alkali Metal Atoms with Tetrahalomethanes. Evidence for a Novel Carbenoid

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Abstract: Reaction of alkali metal atoms with carbon tetrachloride at high dilution in argon deposited at 15°K produced, in addition to trichloromethyl radical, dichlorocarbene, and the carbenoid Cl_3CM , a new carbenoid species identified as a dichlorocarbene-metal halide complex. Infrared examination of the matrix-isolated complex indicated a nonrandom orientation of the two components. Analysis of the effect of the metal atom, the carbon isotope, and the halide ion dependence of the spectrum allowed the determination that the new carbenoid involves interaction of the metal ion and the lone pair of the carbene carbon, i.e., $\text{X}^- \cdots \text{M}^+ \cdots \text{CCl}_2$.

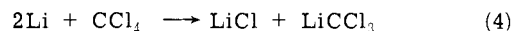
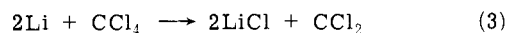
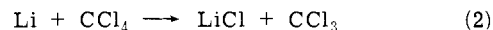
The application of α -elimination routes to the generation of carbenes¹ in solution remains a favored method in spite of ambiguities encountered in interpreting the results of trapping experiments. These ambiguities arise from similarities in reactivity between free divalent carbon species (*carbenes*) and, for example, the α -haloorganometallics generated by metalation of an alkyl halide.² Species of this latter type have been included in a class of reactive intermediates termed *carbenoids*³ which include not only the structurally well-defined α -haloorganometallic reagents just mentioned but also less well-defined carbene-alkali halide complexes of various (usually unstated) degrees of aggregation as well as complexes between α -haloorganometallics and alkali halides. Considerable progress has been made in understanding a carbene-carbenoid relationship in the case of the dichlorocarbene-trichloromethylithium equilibrium (eq 1).



The position of equilibrium lies heavily to the side of trichloromethylithium at -100° .⁴ Reaction with olefins, however, to afford 1,1-dichlorocyclopropanes appears to involve only CCl_2 and not Cl_3CLi since the pattern of reactivity vs. olefin structure is identical with that observed using free CCl_2 generated in the gas phase.⁵ While it may be convenient to envision a continuum of complexes between free dichlorocarbene plus lithium chloride at one extreme and trichloromethylithium at the other, it is much more instructive to probe for those arrangements which correspond to energy minima.

Infrared spectroscopy in association with matrix isolation techniques has proved to be valuable in studies of structure and bonding of the dihalocarbenes and trihalomethylith-

iums generated by the reaction of tetrahalomethanes with alkali metal atoms in solid argon (eq 2-4).⁶



Matrix-isolated CCl_2 generated according to eq 3 is readily identified by comparing vibrational frequencies with CCl_2 generated by photochemical routes⁷ and by thermolysis of phenyltrichloromethylmercury.⁸ Association of lithium chloride molecules with CCl_2 or with LiCCl_3 in the same matrix site is also possible but has so far not been systematically studied. It is of chemical interest to examine the infrared spectra of dichlorocarbene-alkali halide "complexes" to determine: (a) the extent of interaction of the two species when trapped together; and (b) whether the perturbation of CCl_2 vibrations by alkali halides corresponds to a unique and determinable orientation of the two species.

Experimental Section

Matrix reactions of CCl_4 , $^{13}\text{CCl}_4$, CCl_3Br , and CCl_2Br_2 with Li, Na, K, or Cs atoms were performed using experimental techniques described previously.⁹ Matrix samples ($\text{Ar}/\text{CCl}_4 = 100:1$ to $400:1$) were codeposited with alkali metal vapor beams on a CsI substrate maintained at 15°K . Infrared spectra were recorded during and after sample deposition on a Beckman IR-12 spectrophotometer. Wave-number accuracy is $\pm 1 \text{ cm}^{-1}$.

Results and Discussion

Pertinent portions of the infrared spectra obtained on reaction of CCl_4 with ^6Li , Na, K, and Cs atoms in solid

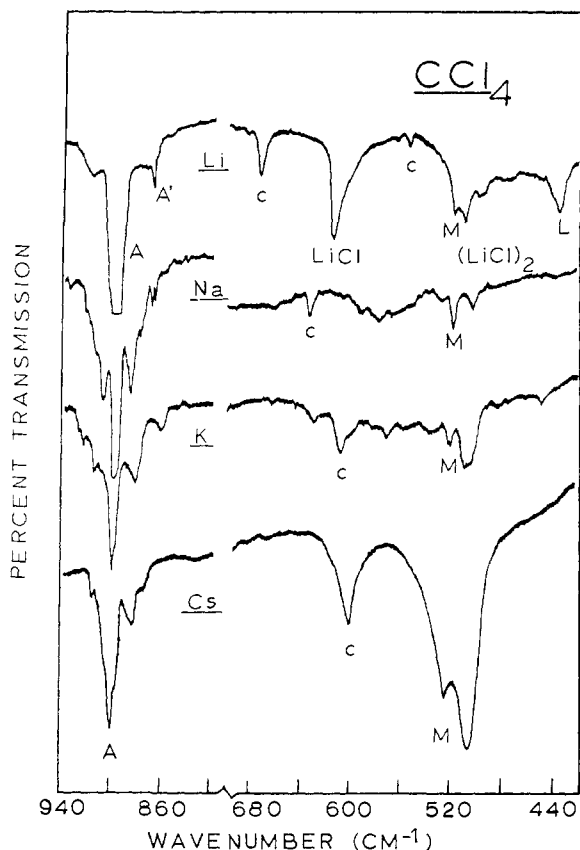


Figure 1. Infrared spectra in the 440–680 and 860–940 cm^{-1} regions following codeposition of ${}^6\text{Li}$, Na, K, and Cs atoms at 14°K with CCl_4 at high dilution in argon.

argon at 15°K are presented in Figure 1. The very intense band at 898 cm^{-1} (A) has been assigned to ν_3 of CCl_3 .⁹ The band at 869 cm^{-1} (A') is the natural abundance ${}^{13}\text{C}$ counterpart of A. The band at 674 cm^{-1} (C) in the lithium trace was incorrectly assigned previously⁹ to ν_1 of CCl_3 ; this band is significant in succeeding discussions. Not shown in the figure are an intense doublet at 745.7–743.7 cm^{-1} and a weak doublet at 719.5–716.7 cm^{-1} which were observed in similar experiments and assigned to ν_3 and ν_1 , respectively, of CCl_2 .^{6a} Consistent with the stoichiometry of eq 3 is the observation that CCl_2 formation was favored relative to CCl_3 at high lithium atom concentrations. The bands labeled M and L correspond to LiCCl_3 species (and analogously for the other alkali metal atoms)^{6c} and were also favored at high lithium atom concentrations.

An important feature of the spectra shown in Figure 1 is the contrasting effect of changing metal reagents on the spectrum. The intense 898- cm^{-1} CCl_3 band was produced unshifted; the shoulders observed with the heavier alkali reagents are attributed to $\text{MCl}\cdots\text{CCl}_3$ complexes. The M band was also unshifted; this absorption is due to the ν_3 intraionic mode of CCl_3^- in the M^+CCl_3^- species. Of primary interest here is the progressive shift of the C band from 674–634 to 608–603 cm^{-1} when the metal reagent was altered. Table I lists the C-band frequencies for all the reagents used. Clearly this species involved the alkali metal reagent.

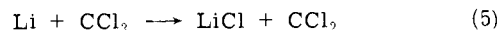
In lithium atom matrix reactions with CBr_4 , sharp bands observed at 641 and 596 cm^{-1} were assigned to ν_3 and ν_1 , respectively, of CBr_2 .^{6b} Of particular interest here, a band was observed at 582 cm^{-1} which is the bromine counterpart of the 674- cm^{-1} C band. This feature was incorrectly^{6b} assigned earlier to CBr_3 .

Table I. Wave Numbers Observed for the C Bands Assigned to the Antisymmetric C–Cl₂ Vibration of an $\text{X}^-\cdots\text{M}^+\cdots\text{CCl}_2$ Species^a

Reagents	C, cm^{-1}
${}^6\text{Li} + \text{CCl}_4$	674.5
${}^7\text{Li} + \text{CCl}_4$	674
${}^6\text{Li} + \text{CCl}_4, {}^{13}\text{CCl}_4$	674.5, 654.0
Na + CCl_4	634.6
Na + $\text{CCl}_4, {}^{13}\text{CCl}_4$	634.0, 614.5
K + CCl_4	608.3
K + $\text{CCl}_4, {}^{13}\text{CCl}_4$	608, 590
Cs + CCl_4	603
${}^7\text{Li} + \text{CCl}_2\text{Br}$	675
Na + CCl_2Br	634.5
${}^6\text{Li} + \text{CCl}_2\text{Br}_2$	675

^a The analogous mode of free CCl_2 appeared at 745.7 cm^{-1} in solid argon.

As was the case with bands assigned to CCl_2 , the C band is favored at higher metal concentrations and, like CCl_2 , is associated with a species resulting from reaction of metal atoms with the primary reaction product CCl_3 . The C band becomes progressively more intense compared with that of CCl_2 with increasing metal atomic weight. This is consistent with the C band arising from a carbene-alkali metal chloride complex where the heavier MCl molecules are less likely than the lighter ones to diffuse away from the carbene before condensation of the two products of eq 5 in the same matrix site.



The weak band at 555 cm^{-1} in the ${}^6\text{Li}$ spectrum might be the ${}^6\text{Li}$ -Cl vibration in the complexed carbene species, **1**. Unfortunately, the ${}^7\text{Li}$ counterpart could not be observed owing to overlapping of the strong M bands.

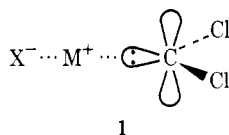
It can be shown that the species responsible for the band labeled C contains one carbon atom by allowing 51% ${}^{13}\text{C}$ -enriched CCl_4 to react in separate experiments with ${}^6\text{Li}$, Na, and K. The appearance of C as a doublet in each case establishes the species as the carrier of a single carbon atom.

In contrast to the dependence of the frequency of C on the nature of the alkali metal atom, the C band position does not depend on its halide counterion. In experiments with bromotrichloromethane and ${}^7\text{Li}$ (or Na), CCl_2 was formed with either one molecule of LiCl (or NaCl) or LiBr (or NaBr) nearby. Dichlorodibromomethane experiments produced the 675- cm^{-1} C band with weak but observable intensity. In this case, LiBr must be in an adjacent matrix site. The absence of observable splitting or wave-number shift of the C band indicates minimal interaction of the halide ion with the absorbing species.

It is apparent from the data presented that the species responsible for the C band is a dichlorocarbene which is perturbed by an alkali metal halide molecule in a way which corresponds to a nonrandom orientation of CCl_2 and M^+X^- , i.e., a carbenoid of defined structure.

The previously reported^{6a} isotopic data for ν_3 of CCl_2 provide ample basis for calculating the valence angle of free dichlorocarbene. The ${}^{12}\text{C}$ and ${}^{13}\text{C}$ isotopic ν_3 frequencies, 745.7 and 723.2 cm^{-1} , provide a lower limit of $100 \pm 9^\circ$; the ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$ ν_3 frequencies, 745.8 and 741.7 cm^{-1} , give a $111 \pm 7^\circ$ upper limit.⁸ The upper limit-lower limit average of 106° provides a good measure of the bond angle for isotopes where anharmonicities are nearly the same. The corresponding ${}^{12}\text{C}$ - ${}^{13}\text{C}$ isotopic shift data for ν_3 of the LiCl -, NaCl -, and KCl -complexed dichlorocarbene predict a Cl-C-Cl angle with a lower limit of 100° . As nearly as can be determined, therefore, association of the alkali metal chloride and dichlorocarbene does not alter the geometry of the carbene partner.

Of the numerous orientations which are possible for the components of a dichlorocarbene-metal halide complex, the structure shown (**1**) is most consistent with the data and makes the best chemical sense.



Coordination of the metal ion to CCl_2 involves the lone pair of the carbene and perturbs the carbon-chlorine vibrational frequencies by an amount which is dependent on the metal ion and independent of the halide ion. Involvement of the carbon lone pair rather than chlorine lone pairs is indicated by the near constancy of the Cl-C-Cl valence angle in free and complexed dichlorocarbene. It is also of interest that the complexation described by **1** is similar to that tentatively suggested earlier ($\text{Cl}_2\text{C}^+\text{LiCl}^-$) by Closs¹⁰ as being in equilibrium with trichloromethylithium.

Conclusions

The carbenoid species produced by association of dichlorocarbene and alkali metal halides appear to be of two distinct types. There is, in addition to the previously described MCCl_3 , a complex of the type $\text{X}^- \cdots \text{M}^+ \cdots \text{CCl}_2$ (**1**) proposed here on the basis of matrix isolation infrared studies. The extent to which **1** is important in generation and reac-

tions of carbenes and carbenoids in solution remains to be seen. It is likely that **1** would be more electrophilic than either CCl_2 or MCCl_3 , a property subject to experimental testing.

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