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ON THE INFRARED SPECTRA OF DICHLOROCARBENE AND THE TRICHLOROMETHYL RADICAL IN SOLID ARGON

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We have announced the infrared detection(1) of ν_3 of the CCl_3 radical and recently discussed the infrared spectra (2,3) of the products of reactions of lithium atoms with carbon tetrachloride observed when molecular beams of the alkali metal and halocarbon at high dilution in argon are simultaneously condensed on a salt window at 15°K. Since we were not aware of the pyrolysis and discharge work of Steudel(4) at the writing of these earlier papers, we feel that it is now necessary to question the interpretation presented by Steudel.

Steudel passed gas streams of CCl_4, C_2Cl_6, $HCCl_3$ and $SCCl_2$ through a pyrolysis (900°C) or discharge tube and onto a salt window at 83°K where he observed a new absorption at 896 cm^{-1} which could not be attributed to any stable chlorocarbon material. Since both C_2Cl_6 and C_2Cl_4 reaction products were found for each of Steudel's precursors, both CCl_3 and CCl_2 intermediates are likely to be present. Because CCl_3 is expected to be pyramidal, Steudel feels that 896 cm^{-1} is too high a frequency for assignment to CCl_3, so he assigns this absorption to ν_3 of CCl_2.

In reactions of lithium atoms with carbon tetrachloride(1,2), we observe a very intense absorption at 897.8 ± 0.5 cm^{-1} which has a ^{13}C counterpart at 869.0 ± 0.5 cm^{-1}. When the various perbromochloromethane(2) parent materials are deposited with lithium atoms, we observe bands due to LiCl and LiBr and the sharp, intense absorptions with assignments shown in Table I. The presence of both LiCl and LiBr suggests that two different trihalomethyl radicals were produced, depending upon whether a bromine or chlorine atom is abstracted from the parent perbromochloromethane by the lithium atom. In the CCl_3Br experiments in addition to the intense 898 cm^{-1} band, we observe intense absorptions at 888 and 835 cm^{-1} which suggests that the 898 cm^{-1} absorption is doubly degenerate and the 888 and 835 cm^{-1} absorptions result when this degeneracy is split by substitution of bromine for a chlorine atom. The same 888 and 835 cm^{-1} absorptions are observed when the CCl_2Br_2 parent material is used, along with new bands at 856 and 783 cm^{-1}. The 856 and 783 cm^{-1} bands are produced from $CClBr_3$ with a new band at 773 cm^{-1} which is also produced from the CBr_4 parent as Table I shows. The 888 cm^{-1} absorption shows chlorine isotopic splittings with intensities appropriate for a species containing two equivalent chlorine atoms while the 856 cm^{-1} band is a doublet whose intensities suggest that a single chlorine atom is present in this absorber. The 835 and 783 cm^{-1} absorptions exhibit no splittings so these vibrations must primarily involve

Table I. Absorptions (cm^{-1}) observed in an argon matrix at 15°K in the 770-900 cm^{-1} spectral region for reactions of lithium atoms with tetrahalomethanes.

Parent	CCl_3	CCl_2Br	$CClBr_2$	CBr_3
51% $^{13}CCl_4$	898, 869			
CCl_4	898			
CCl_3Br	898	888, 835		
CCl_2Br_2		888, 835	856, 783	
$CClBr_3$			856, 783	773
CBr_4				773

bromine motions. The absorptions assigned in Table I show that the 898 cm^{-1} frequency is due to a species containing three equivalent chlorine atoms since four different trihalomethyl radicals are observed.

Further evidence for this assignment is found upon warming the deposited sample to 45°K and recooling to 15 °K which allows controlled diffusion of the trapped species. In this operation the 898 cm^{-1} absorption decreases while an absorption due to C_2Cl_6 grows in at 684 cm^{-1}. Force-constant calculations(1) also support the assignment of the 898 and 869 cm^{-1} frequencies of $^{12}CCl_3$ and $^{13}CCl_3$, respectively, to ν_3 the asymmetric carbon-chlorine stretching vibration. The symmetric stretch (ν_1 = 674 cm^{-1}) for CCl_3 is observed (2) which indicates that the radical is pyramidal since this vibration is not infrared active for the planar symmetric species.

We observed absorptions at 745.7 and 719.5 cm^{-1} and their carbon-13 counterparts which show chlorine isotopic splittings with relative intensities appropriate to a species containing two equivalent chlorine atoms. Upon sample warming to 40°K, these absorptions disappear completely while absorptions due to C_2Cl_4 appear. These assignments to ν_3 (745.7 cm^{-1}) and ν_1 (719.5 cm^{-1}) of $^{12}C^{35}Cl_2$ are supported by normal-coordinate calculations using all of the isotopic frequencies, which also give a Cl-C-Cl bond angle of 100°.

The dichlorocarbene was produced by a secondary reaction of lithium atoms with trichloromethyl radicals. Milligan and Jacox (5) have photolysed cyanogen azide in an argon matrix in the presence of chlorine molecules and reported absorptions at 748 and 721 cm^{-1} which they assign to CCl_2 made by the reaction of photolytically produced C atoms with Cl_2. The agreement between the independent assignments of Andrews(3) and Milligan and Jacox(5) to CCl_2 using different methods of production conclusively supports the validity of their assignments and suggests a reinterpretation of Steudel's 896 cm^{-1} absorption.

The 896 cm^{-1} absorption (4) observed by Steudel in a chlorocarbon matrix at 83°K is likely due to the same species as our absorption at 898 cm^{-1} in an argon matrix at 15°K, since such a small difference in matrix shifts is reasonable. We have clearly shown that our 898 cm^{-1} absorber is the trichloromethyl radical, and we suggest that Steudel's 896 cm^{-1} band is also due to CCl_3.

As we have discussed (2,6), the CCl_3 and CBr_3 radicals are known to be resonance stabilized which can account for the fact that ν_3 is somewhat higher than expected on the basis of C orbital hybridization in the species alone. We also point out that principal force constants (3,7) for CCl_2 and CBr_2 are slightly lower than their carbon tetrahalide counterparts which suggests that single bonds are present in the dihalocarbenes and that apparently, there is no appreciable amount of electron donation to the electron defficient carbon leading to pi bond formation.

REFERENCES

1. L. Andrews, J. Phys. Chem. 71, 2761 (1967).
2. L. Andrews, J. Chem. Phys., "Infrared Spectrum of the Trichloromethyl Radical in Solid Argon," to be published.
3. L. Andrews, J. Chem. Phys., "Infrared Spectrum of Dichlorocarbene in Solid Argon," to be published.
4. R. Steudel, Tetrahedron Letters No. 19, 1845 (1967).
5. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 703 (1967).
6. L. Andrews and T. G. Carver, J. Chem. Phys. "Infrared Spectrum of the Tribromomethyl Radical in Solid Argon," to be submitted.
7. L. Andrews and T. G. Carver, J. Chem. Phys., "Infrared Spectrum of Dibromocarbene in Solid Argon," to be submitted.