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Reactions of Alkali-Metal Atoms with Carbon Tetrabromide. Infrared Spectra and Bonding in the Tribromomethyl Radical and Dibromocarbene in Solid Argon

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Simultaneous condensation at 15°K of beams of lithium atoms and carbon tetrabromide diluted in argon produces infrared absorptions which are identified as lithium bromide and the tribromomethyl radical. Comparisons within the series of radicals CCl₂, CCl₂Br, CClBr₂, and CBr₂ verify the molecular identity. Assignments to the carbon-bromine stretching vibrations are $v_1 = 582$ cm⁻¹ and $v_3 = 773$ cm⁻¹, whereas the bending modes ν_2 and ν_4 were not observed. The stretching force constants $F_r = 3.55$ mdyn/Å and $F_{rr}=0.70$ mdyn/Å are compared with those of other bromocarbons and BBr_a. The high carbonbromine stretching-force constant can be rationalized by the fact that the tribromomethyl radical is resonance stabilized. Secondary reaction of lithium atoms with the tribromomethyl radical yields a sufficient concentration of dibromocarbene for infrared spectral study. Variation of the perbromochloromethane precursors and loss of CBr2 absorptions with attendant growth of the most intense C2Br4 absorption on sample warming furnish convincing evidence that dibromocarbene is isolated in the argon matrix. Assignments to the carbon-bromine stretching vibrations are $\nu_1 = 595.0 \text{ cm}^{-1}$ and $\nu_2 = 640.5 \text{ cm}^{-1}$, and the bending mode was not detected. The stretching-force constants $F_r=2.38$ mdyn/Å and $F_{rr}=0.18$ mdyn/Å indicate that C-Br single bonds are present in dibromocarbene, making it unlikely that the electron deficiency of the carbon atom is relieved by pi bonding with bromine.

The tribromomethyl radical and dibromocarbene intermediates have been proposed in a number of reaction mechanisms. In early work, visible-light irradiation of carbon tetrabromide in carbon tetrachloride solution with olefins produced 1-tribromomethyl-2bromoalkane addition products where the proposed mechanism involves the tribromomethyl radical as an intermediate.1 Later studies on gamma radiolysis of carbon tetrabromide in the presence of olefins also vields similar tribromomethyl radical addition products.² A number of authors³⁻⁶ have studied the reaction of olefins with dibromocarbene produced by the basic hydrolysis of bromoform. Recent infrared studies⁷⁻⁹ of reactions of alkali metal atoms with carbon tetrachloride have identified the trichloromethyl radical and dichlorocarbene. Comparison of C-Cl force constants calculated in this work⁸⁻⁹ suggests that the high force constant for CCl₃ is reasonable in view of the earlier proposed¹⁰⁻¹¹ resonance stabilization of the trichloromethyl radical while the force constant for CCl₂ is near single-bond values which implies that no pi bonding is present in dichlorocarbene. As an extension of this work, we have prepared CBr₃ and CBr₂ for spectral study using the matrix reaction of lithium atoms and carbon tetrabromide in order to provide more information on the structure and bonding in these interesting chemical species.

EXPERIMENTAL

The 15°K refrigeration system, lithium-atom source, and experimental technique have been described in detail.8 Samples of carbon tetrabromide in argon $(Ar/CBr_4 \approx 200/1 \text{ to } 600/1)$ were simultaneously condensed with an atomic beam of lithium (Li/CBr₄ \approx ½ to ⅔).

Carbon tetrabromide (Matheson, Coleman and Bell, reagent grade) was recrystallized five times from ethanol and sublimed to remove impurities. The solid CBr₄ was outgassed several times by cooling under vacuum with a dry-ice-acetone bath. Chlorotribromomethane was synthesized according to Dehn¹² using bromoform (Eastman, white label) and sodium hypochlorite (commercial household bleach) and purified in the same manner as the CBr₄.

Since these precursors are known to be unstable, they were used immediately after purification. The vapor pressure of solid CBr4 was estimated to be near 0.9 torr at 25°C by extrapolation of tabulated data,¹³ and the vapor pressure of solid CClBr₃ was measured to be 1 torr at 25°C. Samples were prepared by allowing the solid to vaporize under vacuum into a 3-liter bulb until equilibrium was reached at room temperature,

¹ M. S. Kharasch, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc. 69, 1100 (1947)

² R. Rabilloud, Bull. Soc. Chim. France 1965, 2149. ³ P. S. Skell and A. Y. Garner, J. Am. Chem. Soc. 78, 3409

^{(1956).} ⁴ W. v. E. Doering and P. La Flamme, J. Am. Chem. Soc. 78, 5447 (1956). ⁶ P. S. Skell and A. Y. Garner, J. Am. Chem. Soc. 78, 5430

^{(1956).}

<sup>(1950).
&</sup>lt;sup>6</sup> W. v. E. Doering and W. A. Henderson, Jr., J. Am. Chem. Soc.
80, 5274 (1958).
⁷ L. Andrews, J. Phys. Chem. 71, 2761 (1967).
⁸ L. Andrews, J. Chem. Phys. 48, 972 (1968).
⁹ L. Andrews, J. Chem. Phys. 48, 979 (1968).
¹⁰ N. Davidson and J. H. Sullivan, J. Chem. Phys. 17, 176

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¹¹ M. Szwarc and A. H. Sehon, J. Chem. Phys. 19, 656 (1951).

¹² W. M. Dehn, J. Am. Chem. Soc. 31, 1220 (1909).

¹³ Bolas and Groves, J. Chem. Soc. 24, 773 (1871).



FIG. 1. Infrared spectra recorded in the 350-875-cm⁻¹ spectral region for Ar/CBr₄ deposited at 15°K without lithium and with lithium-6 and lithium-7, and for Ar/CClBr₃ with lithium-6 (truncated bands indicate 0% transmission for that spectrum).

and subsequently adding argon using standard manometric techniques.

Infrared spectra were recorded on a Beckman IR-12 filter-grating spectrophotometer in the 200-4000-cm⁻¹ region. Integrated intensity measurements were made on absorption bands no greater than 90% absorbing, recorded under high resolution conditions of a 3-cm⁻¹/min scanning speed and a scale expansion of 10 or 20 cm⁻¹/inch. Frequency accuracy is ± 0.5 cm⁻¹ and spectral slitwidths were 0.8 cm⁻¹ at 900 cm⁻¹, 0.9 cm⁻¹ at 700 cm⁻¹, and 2.1 cm⁻¹ at 500 cm⁻¹.

RESULTS

Carbon tetrabromide. Figure 1 illustrates spectra recorded in the 350-875-cm⁻¹ region for a sample of Ar/CBr₄ without lithium and with lithium-7 and lithium-6. The absorptions and optical densities are listed in Table I. The spectrum recorded for carbon

tetrabromide deposited without lithium shows the intense ν_8 of the CBr₄ precursor labeled P and weak impurity absorptions labeled I which indicates that our purification of the original CBr₄ sample was reasonably effective. When lithium is deposited with the argon-carbon tetrabromide sample, many new absorptions appear showing that reaction certainly does occur.

The bands labeled LX at 540 cm⁻¹ in the ⁶Li and at 504 cm⁻¹ in the ⁷Li spectra compare with absorptions at 540 and 501 cm⁻¹ in solid argon assigned by Schlick and Schnepp¹⁴ to ⁶LiBr and ⁷LiBr, respectively. This agreement verifies that bromine is abstracted from the parent bromocarbon by the lithium atom.

The weak bands labeled T are attributed to trace absorbers which appear in some but *not all* experiments in this work and also in the earlier carbon tetrachloride

¹⁴ S. Schlick and O. Schnepp, J. Chem. Phys. 41, 463 (1964).

TABLE I. Absorptions (cm⁻¹) recorded in Fig. 1 with optical densities shown parenthetically.

Fig. 1 Identifi- cation	CBr₄ no Li	CBr₄ ″Li	CBr₄ ⁰Li	CClBr ₃ ⁶ Li
C_1				856(0%T)
Т		699(0.12)	839(0.10)	839(0.03)
C_1'				826(0.03)
Ι	795(0.03)	795(0.12)		
S				788(0.1)
C_2				783(0%T)
I, S	777(0.04)	779(0.15)	779(0.1)	779(0.1)
D_1		773(0%T)	773(0%T)	773(0% T)
Ι, Ρ	752(0.17)	752(0.03)	752(0.05)	752(0% T)
D_1', I		746(0.02)	743(0.15)	737(0.1)
I, P'	735(0.20)	735(0.07)	735(0.03)	727(0.03)
Р	675(0% T)	675(0% T)	675(0% T)	683(0% T)
Ι			656(0.04)	656(0.07)
G_1		641(0.11)	641(0.46)	641(0.70)
C 3				620(0.06)
LX				616(0.12)
F_2				612(0.12)
G_2			595(0.03)	595(0.045)
D_2		582(0.04)	582(0.13)	582(0.10)
Т			507(0.07)	575(0.05)
LX		504(0.15)	540(0.22)	540(0% T)
Ι				519(0.06)
T			494(0.05)	494(0.04)
М				473(0.6)
М		462(1.0)	462(0% T)	462(0% T)
I, L	421(0.05)			404(0.20)
Ĺ	. ,	377(0.07)	391(0.13)	391(0.1)

study.⁸ Obviously, such bands are not assignable to a major reaction product, so we are left with the new absorptions labeled D, G, M, and L.

Note added in proof: A careful study of the matrix reaction of lithium atoms with oxygen molecules ($^{16}O_2$ and $^{18}O_2$) has shown that the 795- and 699-cm⁻¹ bands in the ⁷Li spectrum in Fig. 1 and their counterparts at 839 and 743 cm⁻¹ and the 507-cm⁻¹ absorption in ⁶Li spectra are due to binary lithium-oxygen species. Oxygen probably present in trace amounts in the argon matrix gas and the slow ($\sim 3 \times 10^{-6}$ torr/min) leak rate of the vacuum vessel provide O₂ for the lithium reaction. The 699- and 743-cm⁻¹ bands are due to the species Li-O-O which will be discussed in detail in a later publication.

The integrated intensities of the D_1 and D_1' absorptions in the second spectrum in Fig. 1 measured before the very intense D_1 band became completely absorbing are 1.93 ± 0.20 and 0.022 ± 0.004 (cm⁻¹×o.d.), respectively. The relative intensities suggest that the D_1' band is the naturally occurring (1.1%) carbon-13 counterpart of the very intense D_1 absorption. This weak D_1' band does not appear in the spectrum (see Fig. 1) of material from the same sample deposited

without lithium in the immediately following experiment, so the D_1' band must be produced by the lithium reaction.

Chlorotribromomethane. The last spectrum in Fig. 1 was recorded for a sample of Ar/CClBr₃ deposited with lithium-6. As Table I shows, the same D, G, M, and Lbands were observed along with additional M' and L'absorptions at 473 and 404 cm⁻¹, respectively. Two new bands C_1 and C_2 are noted at higher frequencies than D_1 along with new C_3 and F_2 absorptions. The same C_1 and C_2 bands were produced from the CCl₂Br₂ precursor discussed in the lithium-carbon tetrachloride paper.⁸ The C_1 band is a doublet whose components have relative intensities of 3 to 1.

Figure 2 illustrates detailed spectra in the 580-750cm⁻¹ region for samples of argon and CCl₃Br, CClBr₃, and CBr₄ deposited with lithium. Impurity bands present in the precursor are labeled *I*. The G_1 absorption at 641 cm⁻¹ was also observed when the CCl₂Br₂ parent was used, but parent bands obscured the regions of the *F* bands. The *F* bands were not observed when the CCl₄ or CBr₄ precursors were used.

Alkali metal. When sodium is used instead of lithium as a reactant, there is a marked decrease in the intensities of the G absorptions and increase in the M absorption intensity relative to that for the D absorption, which shows that the D, G, and M absorptions are caused by three different molecular species. The D, G, and M absorptions have no measurable lithium isotope



FIG. 2. Infrared spectra recorded in the 580-750-cm⁻¹ spectral region for CCl₃Br, CClBr₈, and CBr₄ samples in argon deposited at 15°K with lithium.

effect nor shift from use of lithium to sodium. The band L at 391 cm⁻¹ for ⁶Li shifts to 377 cm⁻¹ when ⁷Li is used, whereas no sodium counterpart of the L absorption is observed.

Concentration Variation. An increase in the concentration of lithium in the deposited sample causes a corresponding increase in the intensities of the G, M, and L absorptions relative to the D-band intensities. Throughout the various experiments, the ratio of the intensities of the D_1 and D_2 absorptions remains constant at 13 ± 1 , and the G_1 and G_2 absorptions maintain constant relative intensities at 18 ± 2 as Tables II and III show. Likewise, the F_1 and F_2 absorptions maintain approximately constant relative intensities in two experiments.

Diffusion Experiments. Upon warming of the sample deposited at 15°K to 45°K and recooling to 15°K, the G_1 and G_2 absorptions disappear completely, the M and L bands decrease in intensity by about onehalf, while the D_1 and D_2 absorptions remain unchanged except for the disappearance of the sharp weak-satellite bands labeled S on the high-frequency side of the intense D_1 and C_2 absorptions. Similar behavior is noted on sample warming for a weak-satellite band on the high-frequency side of the intense absorption due to the CCl₃ radical in the lithium-carbon tetrachloride study.⁸ Thus, the S bands are attributed to the same species responsible for the very intense nearby absorption trapped in a less stable matrix site which is annealed away upon sample warming. Loss of the Gabsorptions is accompanied by the appearance of a sharp ($\nu_{1/2}=1.5 \text{ cm}^{-1}$, 0.06 o.d.) absorption at 762.5 cm^{-1} which is attributed to C_2Br_4 since the most intense infrared absorption of C2Br4 in the CS2 solution spectrum appears at 766 cm^{-1,15} Warming of the CCl₃Br sample in Fig. 2 to 40°K caused the E_1 and F absorptions to disappear. The E_1 absorption has been assigned to v3 of dichlorocarbene.9 No absorption was detected which could be assigned to C_2Br_6 since we were unable to decrease the D absorptions appreciably before the entire sample annealed and began to vaporize. The diffusion experiments also indicate that

TABLE II. Relative integrated intensities of the D absorptions in different experiments (intensities in $cm^{-1} \times o.d.$).

Parent	D_1 773.0 cm ⁻¹	D ₂ 582.0 cm ⁻¹	D_{1}/D_{2}
CBr4	2.60	0.200	13
CBr ₄	1.84	0.135	14
CBr ₄	1.58	0.120	13
CClBr ₈	2.3	0.20	12

¹⁵ D. E. Mann, J. H. Meal, and E. K. Plyler, J. Chem. Phys. **24**, 1018 (1956).

TABLE III. Relative integrated intensities of the G absorptions in different experiments (integrated intensities in $(cm^{-1} \times o.d.)$.

Parent	G_1 640.5 cm ⁻¹	<i>G</i> ² 595.0 cm ⁻¹	G_1/G_2	
CClBr ₃	1.92	0.11	18	
CBr ₄	1.06	0.063	17	
CBr₄	1.31	0.075	18	
CBr ₄	1.63	0.081	20	
CClBr ₃	1.26	0.075	17	
CClBr ₃	1.44	0.084	17	
CBr ₄	1.76	0.11	16	

the D, G, and M bands are due to three different absorbers.

DISCUSSION

Our present task is to identify absorptions which can be assigned to the tribromomethyl radical and dibromocarbene and to use this data to determine the vibrational potential function and structure of CBr_3 and CBr_2 .

 CBr_3 Identity. The D, G, and M absorptions display distinctly different relative intensities when sodium is used instead of lithium, and on sample warming, so these bands must be due to three different molecular absorbers. The G, M, and L absorptions are favored relative to the D absorptions at high lithium concentrations. Diffusion experiments indicate that the G bands are due to a smaller molecular species which will be discussed in the following section. Consideration of spectra produced by reaction of lithium with the five perbromochloromethane precursors suggests¹⁶ that the M' and L' bands at 473 and 404 cm⁻¹ are due to CClBr₂Li while the 462- and 391-cm⁻¹ M and L bands are caused by CBr₈Li.

The parallel relative-intensity behavior for the D_1 and D_2 bands shown in Table II suggests that both Dbands could be due to the same molecule. The Dabsorptions show no lithium isotope or sodium shift, and they *decrease* in intensity relative to the L absorption which *shows* a lithium shift when the concentration of lithium is increased. This behavior suggests that the D absorber does not contain an alkali-metal atom.

The presence of two new C_1 and C_2 bands in addition to the D_1 band in the CClBr₃ experiment suggests that the D_1 band is doubly degenerate and that the C_1 and C_2 absorptions result when this degeneracy is split by the substitution of chlorine for a bromine atom. Similar behavior has been discussed by Andrews⁸ for CCl₃Br

¹⁶ L. Andrews and T. G. Carver, J. Phys. Chem. 72, 1743 (1968).

along with spectra for all of the perbromochloromethane reactions with lithium. These spectra show that four distinct bromine-chlorine substituted products are produced from the five perbromochloromethane parent materials and that each product is produced from two of the five parent materials depending upon whether a bromine or chlorine atom is abstracted by the alkali-metal atom. The observation of four degrees of bromine-chlorine substitution indicates that three equivalent halogens are present in these product species which are the CCl₃, CCl₂Br, CClBr₂, and CBr₃ radicals. The doubly degenerate D_1 band requires at least C_{3v} symmetry, which shows that the three bromines in species D are equivalent. The relative intensities of the components of the C_1 doublet are in good agreement with the distribution of natural chlorine isotopes, which indicates that the C absorber contains a single chlorine atom. This is consistent with the identification of species C as the CClBr₂ radical.

The presence of three equivalent bromine atoms in species D strongly suggests that a single carbon atom is present since the only simple binary bromocarbon species with three equivalent bromine atoms is CBr₃. Furthermore, the D_1 absorption is very intense and likely due to a primary reaction of CBr₄ which would yield a species containing a single carbon atom. The presence of carbon in species D is verified by the detection of absorption D_1' with appropriate intensity to be due to the naturally occurring carbon-13 isotope. Thus, species D has the formula CBr₃ with the symmetrical structure.

CClBr Identity. Absorptions F_1 and F_2 are observed in the CCl₃Br experiments, while only the F_2 band is recorded using CClBr₃ since the F_1 band is obscured by an impurity. Since the F_1 and F_2 bands maintain approximately constant relative intensities, they are attributed to the same molecular species, which disappears on sample warming to 40°K, as did the dichlorocarbene absorption. The only chemical species common to both CCl₃Br and CClBr₃ which is expected to disappear completely on sample warming is CClBr.

 CBr_2 Identity. The G_1 band is observed when CCl_2Br_2 , $CClBr_3$, and CBr_4 parents are used, while its weaker G_2 counterpart is observed in the experiments using $CClBr_3$ and CBr_4 . The parallel relative intensities of the G_1 and G_2 absorptions shown in Table III suggest that the two G bands are due to the same molecular species. The distinctly different intensity behavior in sodium and sample warming experiments indicates that the G bands are due to a molecular species different from CBr_3 or the M absorber. This chemical evidence shows that the species G contains two bromine atoms and a single carbon atom, the only possibility common to the three parent materials.

The G absorptions show no lithium isotope nor sodium shift, but an increase in lithium concentration increases the G-band intensities relative to the CBr³ absorption intensities. Thus, species G is favored at high lithium concentrations, which suggests that the G absorber is the union of Li and CBr₃ or the result of further reaction of Li and CBr₃ to eliminate LiBr. The loss of the G absorptions with attendant growth of the C_2Br_4 absorptions on sample warming implies that lithium is not present in species G and indicates a preference for the latter possibility.

The chemical evidence and reaction with little or no activation energy to produce C_2Br_4 show that species G has the formula CBr_2 .

The primary reaction in the lithium-carbon tetrabromide study yields LiBr and the CBr₃ radical. These data suggest that dibromocarbene is formed by a secondary reaction of Li and CBr₃.

*CBr*₃ Vibrational Assignment. Since the three bromine atoms are equivalent, the tribromomethyl radical has four distinct fundamental frequencies: ν_1 (a_1 , symmetric stretch), ν_2 (a_1 , symmetric bend), ν_3 (e, asymmetric stretch), and ν_4 (e, asymmetric bend). The symmetric stretch will be the only vibration not active in the infrared if CBr₃ is planar, whereas all four frequencies are infrared active if the species is nonplanar or pyramidal.

We have shown by chlorine substitution that the D_1 band is doubly degenerate, and since the carbon-13 shift for absorption D_1 is appropriate, we assign the 773-cm⁻¹ absorption to ν_3 , the asymmetric C-Br stretching vibration.

The symmetric stretching mode ν_1 is nondegenerate, so we expect to see a single ν_1 absorption for each of the radicals, CCl₃, CCl₂Br, CClBr₂, and CBr₃, as is observed for the corresponding haloforms,¹⁷ if the radicals are nonplanar. The search for the weaker symmetric stretch of the CCl₂Br and CClBr₂ radicals is made more difficult by the fact that two different trihalomethyl radicals are produced from the perbromochloromethane precursors. Nevertheless, the band labeled C_3 at 620 cm⁻¹ on the side of the ⁶LiCl absorption in the last spectrum of Fig. 1 and an analogous band in lithium-7 experiments are assignable to ν_1 of CClBr₂. We were unable to find a band in the 630–655-cm⁻¹ region which could be attributed to ν_1 of CCl₂Br.

The remaining D_2 (582 cm⁻¹) absorption in the C-Br stretching region is assigned to ν_1 of CBr₃ based on its intensity association with ν_1 and production from both CBr₄ and CBr₃Cl. This assignment is supported by comparison of symmetric C-X stretching vibrations for CCl₃ (674 cm⁻¹)⁸ and HCCl₃ (668 cm⁻¹), and CBr₃ (582 cm⁻¹) and HCBr₃ (539 cm⁻¹).¹⁷ The bending modes ν_2 and ν_4 were not observed due to the long-wavelength limits of the CsI optical windows and the spectrophotometer.

CClBr Vibrational Assignment. The CClBr molecule

¹⁷ G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Company, Inc., New York, 1945), p. 320, has C_s symmetry with three infrared allowed vibrations. Table IV contrasts dihalocarbene and methylene halide frequencies and suggests that the 739-cm⁻¹ absorption is the C-Cl stretching vibration and the 612-cm⁻¹ band is due to the C-Br stretch. No bending mode was observed.

CBr₂ Vibrational Assignment. Dibromocarbene has C_{2v} symmetry if the molecule is bent like $CCl_2^{9,18}$ or $D_{\infty h}$ symmetry for the linear species like triplet methylene. CBr₂ has three distinct vibrational frequencies; however, the symmetric stretch will not be infrared active if the molecule has the linear symmetrical structure. The observation of two bands in the C-Br stretching region provides a symmetric stretching mode and indicates that the molecule is bent. Our assignments to v_1 (a_1 , symmetric stretch) and v_3 (b_1 , asymmetric stretch) are based on comparison of intensities and frequencies with the definitive assign-

TABLE IV. Carbon-halogen stretching frequencies (cm⁻¹) for dihalocarbenes and methylene halides in an argon matrix at 15°K. Frequency accuracy is ± 0.5 cm⁻¹, unless otherwise indicated. Chlorine frequencies are for the most abundant isotope.

CCl ₂ ª	CClBr	CBr ₂	
745.7	739 ± 1	640.5	
719.5	612 ± 1	595.0	
$H_2CCl_{2^b}$	H ₂ CClBr ^b	H ₂ CBr ₂ ^b	
749.2	738.0	650.0	
711.9	611.0	583.3	

⁸ Reference 9.

^b L. Andrews (unpublished results).

ments to v_1 and v_3 of dichlorocarbene⁹ using chlorine isotope splittings. For CCl_2 , ν_3 is higher and eight times as intense as v_1 , which suggests the assignment of the more intense 641-cm⁻¹ band to ν_3 and the weaker 595-cm⁻¹ band to ν_1 of dibromocarbene. This assignment is consistent with the observation that the asymmetric bromine stretch is higher than the symmetric C-Br mode for methylene bromide.¹⁹ The bending mode ν_2 was not observed due to the long-wavelength limit of our instrument.

Normal-Coordinate Calculations. The observation of an absorption assigned to ν_1 of CBr₃ suggests that the radical is nonplanar. We expect the separation of high and low frequencies in a symmetry-coordinate block to be a good approximation for ν_3 (773 cm⁻¹) and ν_4 $(<200 \text{ cm}^{-1})$ and a satisfactory approximation for ν_1 (582 cm⁻¹) and ν_2 (~250 cm⁻¹). The ¹²C and ¹³C assignments to ν_3 were used to calculate F_{33} for assumed Br-C-Br bond angles from 100° to 115°. The discrepancies between the ¹²C and ¹³C force constants minimize at the higher bond angle, but these calculations do not provide a definitive choice for the Br–C–Br

¹⁸ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 703 (1967). ¹⁰ T. Y. Wu, J. Chem. Phys. 10, 116 (1942).

TABLE V. Potential constants and normal-coordinate calculations for CBr₃ using an assumed Br-C-Br angle of 109.5°.

ν_3 observed	ν_3 calculated	v_1 observed
773.0	(773.0)	582.0
745.5	745.7	•••
$F_{11} = 4.96$	0 mdyn/Å	
$F_{33} = 2.84$	7 mdyn/Å	
$F_{33} = 2.84$	6 mdyn/Å	
	ν_3 observed 773.0 745.5 $F_{11}=4.96$ $F_{33}=2.84$ $F_{33}=2.84$	$\begin{array}{c cccc} \nu_3 \text{ observed} & \nu_3 \text{ calculated} \\ \hline 773.0 & (773.0) \\ 745.5 & 745.7 \\ F_{11} = 4.960 \text{ mdyn}/\text{\AA} \\ F_{33} = 2.847 \text{ mdyn}/\text{\AA} \\ F_{33} = 2.846 \text{ mdyn}/\text{\AA} \end{array}$

bond angle due to the approximation involved. Using the separation of frequencies, we calculate the force constants listed in Table V for the tetrahedral Br-C-Br bond angle. Agreement between the ¹²C and ¹³C values of F_{33} is excellent as is the calculated value of ν_3 for ¹³CBr₃ based on the ¹²CBr₃ observed frequency.

The three vibrational frequencies of bromochlorocarbene are all of A' symmetry in the C_s point group. Without any isotopic data, we can only calculate approximate force constants using the diagonal G-matrix elements for the C-Cl and C-Br stretching coordinates. These calculations give $F_{C-Cl} = 2.87$ and $F_{C-Br} = 2.30$ mdyn/Å for bromochlorocarbene. The stretch-stretch interaction force constant is neglected in this calculation; however, it is expected to be small as it is for CCl₂ and CBr₂, since the valence angle in the dihalocarbenes is near 100°.

Dibromocarbene belongs to the C_{2v} point group with v_3 alone in the b_1 symmetry class, while v_1 and v_2 are both a_1 . The Br-C-Br bond angle is assumed to be 100° since this value⁹ was calculated for CCl₂ and it is near the bond angle in CF₂ (105°).²⁰ We expect the separation of high and low frequencies to be a good approximation for ν_1 (595 cm⁻¹) and ν_2 (<200 cm⁻¹). Using symmetry coordinates, we calculate $F_{33} = 2.194$ and $F_{11} = 2.563 \text{ mdyn/Å}$ for dibromocarbene.

CONCLUSIONS

The infrared spectra of the tribromomethyl radical and dibromocarbene are of interest since they provide

TABLE VI. Bromocarbon and BBr₃ force constants, (mdyn/Å).

Molecule	F,	Frr	Reference, v
CBra	3.55	0.70	a.
C ₂ Br ₄	3.25	0.59	b
BBr ₃	2.99	0.33	с
(BBr_s)	(2.74)	(0.46)	d
CBr ₄	2.45	0.30	е
CBr ₂	2.38	0.18	f

^a Calculated in this work assuming Br-C-Br angle =109.5°

^b Reference 15, calculated assuming same X-C-X angle (114°) as for C2Cl4 and C2F4.

⁶ T. Wentink and V. H. Tiensuu, J. Chem. Phys. 28, 826 (1958).

^d Calculated using all frequencies by L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956).

^e R. R. Haun and W. D. Harkins, J. Am. Chem. Soc. 54, 3917 (1932). ^f Calculated in this work assuming Br-C-Br angle = 100°.

²⁰ F. X. Powell and D. R. Lide, Jr., J. Chem. Phys. 45, 1067 (1966).



FIG. 3. Covalent and charged resonance structures for the tribromomethyl radical.

information on the structure, vibrational potential function, and bonding in these chemical intermediates.

Structure. Observation of the symmetric stretching mode ν_1 suggests that CBr₃ radical is pyramidal like its chlorine and fluorine counterparts. However, the integrated intensity of ν_1 detected here is a factor of 13 weaker than ν_3 . It is possible that interactions between CBr₃ and the polar LiBr molecule in an adjacent matrix site could effect the structure of the radical. Nevertheless, we must conclude that the tribromomethyl radical observed here is probably nonplanar.

The assignment of the symmetric C-Br stretching mode of dibromocarbene in this infrared study indicates that CBr_2 is bent like CF_2 and CCl_2 . It is likely that CBr_2 also has the singlet electronic ground state, the same conclusion reached from stereospecific additions of CBr_2 to olefins.^{3,4}

C-Br Force Constant. Combining the symmetry coordinate force constants listed in Table V for CBr₃ give $F_{C-Br}=3.55$ and $F_{C-Br,C-Br}=0.70$ mdyn/Å. These potential constants are listed in Table VI along with those calculated for other bromocarbons and BBr₂ using the separation of frequencies in a symmetry block in order to compare bromocarbon force constants calculated in the same manner. The separation of frequencies gives good approximate force constants, as the comparison for BBr₃ shows. The force constant for CBr₃ is somewhat higher than that for CBr₄, as comparison of the asymmetric stretching vibrations (which have the same *G*-matrix element for the same Br-C-Br bond angle) for CBr₃ ($\nu_3=773$ cm⁻¹) and CBr₄ ($\nu_3=675$ cm⁻¹) suggests.

Combination of the symmetry coordinate force constants F_{11} and F_{33} for CBr₂ gives $F_{C-Br}=2.38$ and $F_{C-Br,C-Br}=0.18$ mdyn/Å. The carbon-bromine stretching force constant for CBr₂ is slightly lower than that for CBr₄ as Table VI shows. The F_{C-Br} (2.30 mdyn/Å) and F_{C-C1} (2.87 mdyn/Å) for bromochlorocarbene are near the values of the respective carbon-halogen force constants for CBr₂ and CCl₂ (2.86 mdyn/Å).⁹

Bonding in CBr_3 . The dissociation energies of hydrogen and bromine bonds to CBr_3 radicals are about 13-17 kcals lower than the dissociation energies for hydrogen and bromine bonds to CH_3 radicals. This information suggests that the CBr_3 radical is resonance stabilized, like its chlorine counterpart. Such stabilization can be explained as resonance between the covalent structure and the three equivalent charged structures illustrated in Fig. 3. Similar structures have been proposed to explain resonance stabilization in the trichloromethyl radical.^{8,10,11}

Resonance stabilization in the CBr₃ radical can help rationalize the fact that the C-Br force constant in CBr₃ is higher than in CBr₄. Participation of the charged resonance structures in Fig. 3 should cause an increase in C-Br bond strength over that of a single covalent bond which leads to an increase in the C-Br force constant over single covalent bond values.

It is interesting to note that the principal force constant for CBr₃ is higher than for C₂Br₄, whereas F_{C-C1} for CCl₃ is slightly less⁸ than for C₂Cl₄. Alphahalo substituents are known to stabilize free radicals²¹ in the order Br> Cl. We might expect more participation of the ionic structures in Fig. 3 for CBr₃ than for CCl₃ due to the fact that Br has a lower electronegativity than Cl which would suggest that the CBr₃ radical might be slightly more resonance stabilized than CCl₃. On this basis, it is not surprising that F_{C-Br} for CBr₃ exceeds that for C₂Br₄, whereas the reverse is true for the chlorine counterparts.

Bonding in CBr_2 . As mentioned above, the carbonbromine force constant for CBr₂ (2.38 mdyn/Å) is near that for CBr₄ (2.45 mdyn/Å) where carbonbromine single bonds are expected. The comparison of dibromocarbene and methylene bromide frequencies in Table IV implies similar carbon-bromine bonding since the hydrogens in H_2CBr_2 make little contribution to the reduced mass of the bromine vibrations. These data suggest that normal C-Br single bonds are present in dibromocarbene and that expected^{5,21,22} electron transfer from one of the bromine atoms to the electron deficient carbon forming a pi bond between carbon and one bromine is apparently not present to any significant degree. Perhaps such electron transfer is made unfavorable by repulsion between the nonbonding electrons on the nonparticipating bromine and the increased electron density on the carbon atom.

Similar bonding is present in dichlorocarbene. The close agreement of the carbon-chlorine frequencies shown in Table IV for dichlorocarbene and methylene chloride and the carbon-chlorine force constant comparison⁹ for CCl₂ (2.86 mdyn/Å) and CCl₄ (3.08 mdyn/Å) support the conclusion that apparently normal carbon-halogen single bonds are present in these dihalocarbenes.

²¹ J. Hine and S. J. Ehrenson, J. Am. Chem. Soc. 80, 824 (1958). ²² W. Kirmse, *Carbene Chemistry* (Academic Press Inc., New York, 1964).