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Infrared Spectrum of the Intramolecular Hydrogen-Bonded Chloroform Anion Cl^-–$HCCl_2$ in Solid Argon at 15 K

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Abstract: The matrix photoionization products of chloroform, including its deuterium and ^{13}C isotopes, and the $CHCl_2Br$ and $CHCl_2I$ compounds have been studied by infrared spectroscopy. The anion product exhibits isotopic data appropriate for a single H, single C, and two equivalent Cl atom species, while bromine and iodine substitution data indicate the involvement of a third inequivalent halogen atom; these observations identify the Cl^-–$HCCl_2$ anion, which is produced upon electron capture by chloroform. The infrared spectrum containing ν_s, $2\nu_b$, ν_b, and ν_x clearly demonstrates the effect of hydrogen bonding in Cl^-–$HCCl_2$, which decreases in the Br^-–$HCCl_2$ and I^-–$HCCl_2$ anions.

Introduction

Thermal electron capture by chloromethanes in the gas phase is generally considered to be a dissociative process giving chloride ion and the appropriate methyl radical. The intermediate parent radical anion in this process is of limited stability since the radical anion electron probably first occupies a σ^*(C–Cl) antibonding orbital and this C–Cl bond is easily dissociated. Direct spectroscopic evidence for parent radical anions of this type is limited to recent ESR studies of CF_3Cl^-, $CF_2Cl_2^-$, and $CFCl_3^-$ following γ-radiolysis of the parent in tetramethylsilane at 101 K,[1] to infrared detection of $CHCl_3^-$ and $CHBr_3^-$ prepared by proton radiolysis of the haloforms during condensation with excess argon at 15 K,[2] and to infrared observation of CF_3Cl^-, CF_3Br^-, and CF_3I^- and the possible infrared detection of $CF_2Cl_2^-$ and $CFCl_3^-$ following argon resonance photoionization of the precursors during condensation with argon at 15 K.[3,4]

The $CHCl_3^-$ radical anion in solid argon readily photodissociated, but the products were not identified.[2] Since hydrogen bonding has been documented for chloroform,[5] the possibility of an intramolecular hydrogen-bonded chloroform anion must be considered for the decomposition product of $CHCl_3^-$ in condensed media. Three infrared matrix isolation studies involving electron capture by chloroform have been reported, but the stable anion product was identified as $CHCl_2^-$ in each case.[6,2,7] We report here a reinvestigation of the chloroform electron capture product, including infrared studies on the bromine and iodine substituted compounds, with a reassignment of the infrared absorptions to the intramolecular hydrogen-bonded anion Cl^-HCCl_2, which is of considerable chemical and spectroscopic interest as a model compound for hydrogen bonding.

Experimental Section

The experimental methods and apparatus have been described in detail elsewhere.[8-10] Samples of chloroform ($CHCl_3$, $CDCl_3$, and $^{13}CHCl_3$), dichlorobromomethane, and dichloroiodomethane in argon (Ar/CHX_3 = 400/1) were condensed on a CsI window at 15 K and simultaneously exposed to an open argon microwave discharge through a 1-mm orifice for 20-h periods. Dichloroiodomethane was synthesized by the reaction of iodoform and mercuric chloride.[11] The solid compounds (10 g of CHI_3 and 14 g of $HgCl_2$) were ground together, placed in a Pyrex tube attached to a vacuum line, and heated to about 95 °C. Dichloroiodomethane was distilled into a cold finger; the liquid product was faint purple owing to the presence of iodine impurity. The matrix sample was prepared by distilling $CHCl_2I$ from $Mg(ClO_4)_2$; infrared spectra showed about 5% $CHCl_3$ impurity. A Beckman IR-12 infrared spectrophotometer was used to record spectra at 8 cm^{-1}/min on expanded wavenumber scale before and after filtered high-pressure mercury arc photolysis of these matrix samples; wavenumber accuracy is ± 0.3 cm^{-1} when reported to the nearest 0.1 cm^{-1} and ± 1 cm^{-1} otherwise.

Results

The infrared spectrum from a $CHCl_3$ experiment is illustrated in Figure 1a. The major product bands at 2723, 2499, 1291, and 1271 cm^{-1}, a triplet at 1038, 1035, and 1032 cm^{-1}, and a doublet at 838 and 836 cm^{-1}, labeled A and C in the figure, are in agreement with the earlier work of Jacox and Milligan (JM).[6,7] Using a 90% carbon-13 enriched $^{13}CHCl_3$ sample, the spectrum in Figure 2a was produced. The carbon-13 product bands shifted to 2714, 2493, 1282, and 1268 cm^{-1}, a triplet at 1013, 1010, and 1007 cm^{-1}, and a doublet at 813 and 811 cm^{-1}, also labeled A and C in the figure; the latter five bands are in agreement with JM, who could not resolve the former broad band into isotopic components with a 55% $^{13}CHCl_3$ sample. The absorption bands and intensities from this 90% ^{13}C experiment are listed in Table I; the observation of both ^{12}C and ^{13}C counterparts of the major product bands with 1:9 relative intensities indicates that the products are single carbon atom species.

High-pressure mercury arc photolysis of the 90% $^{13}CHCl_3$ matrix sample is of particular interest, and the spectra are contrasted in Figure 2. As seen in trace (b), 30 min of 290–1000-nm photolysis had little effect on the C bands, but the A absorptions were decreased by 60%, broad 705- and 974-cm^{-1} bands were markedly increased, and a comparatively sharp 3:1 relative intensity 898.0–891.7-cm^{-1} doublet appeared in the spectrum. The sample was next exposed to the water-filtered arc (220–1000 nm) for 30 min, and the resulting spectrum is shown in Figure 2c; the C bands were reduced by 40%, the A absorptions were slightly increased, while the 974-, 898-, 892-, and 705-cm^{-1} bands were decreased. A final exposure to the water-filtered arc for an additional 100 min reduced all of the

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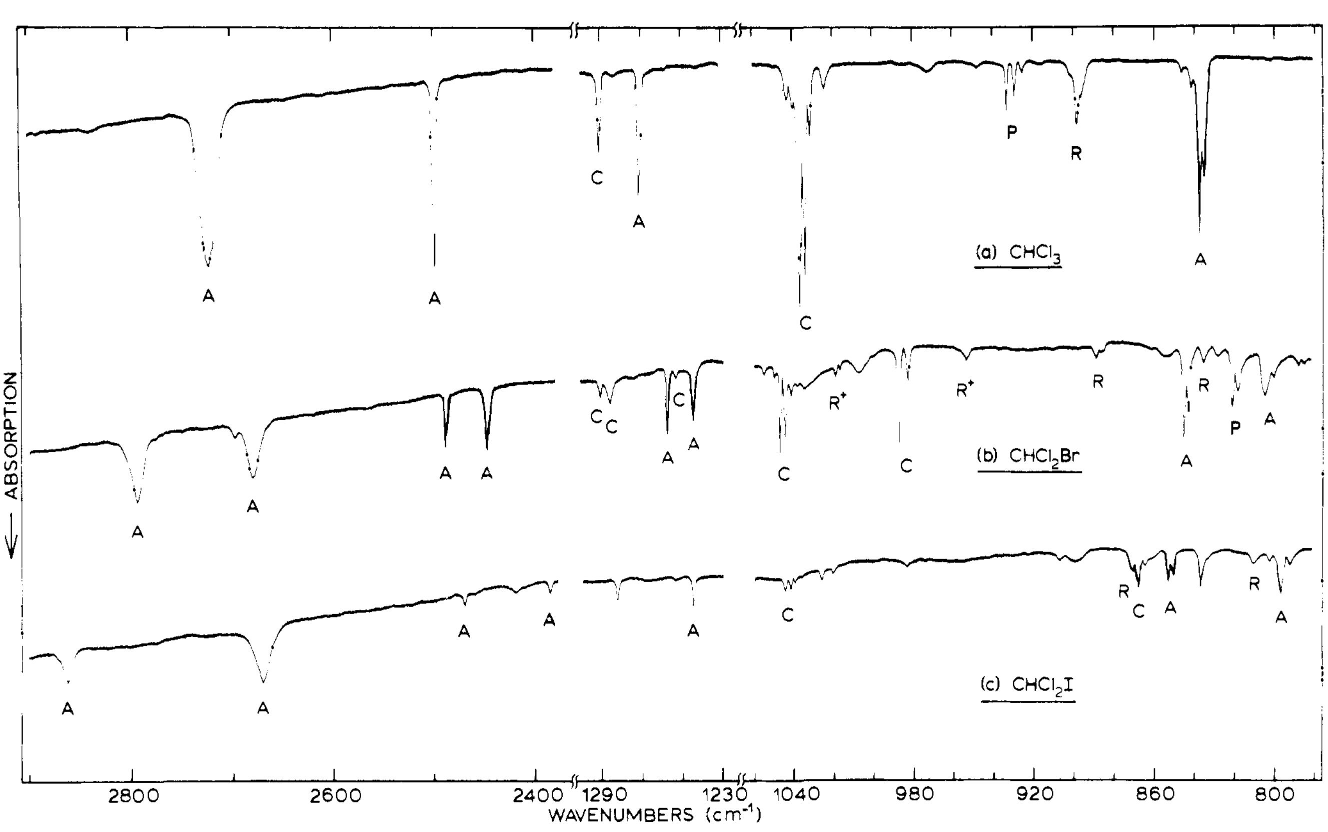

Figure 1. Expanded-scale infrared spectra of dichlorohaloform matrix samples, Ar/$CHCl_2X$ = 400/1, subjected to argon resonance photoionization during condensation at 15 K: (a) $CHCl_3$, (b) $CHCl_2Br$, (c) $CHCl_2I$. The label R denotes CCl_2X radical and R^+ identifies CCl_2X^+ product absorptions.

above product absorptions and *increased* bands at 1003, 904 and 870 cm^{-1}, due respectively to $^{13}CCl_3^+$, Ar$_n$H$^+$, and $^{13}CCl_3$,[6,8,10,12,13] as shown in Figure 2d. The natural isotopic $CHCl_3$ experiment was photolyzed by the high-pressure mercury arc with analogous results; 340-600-nm photolysis reduced the A bands by 20% and produced new 705-, 918.0-, 924.0-, and 974-cm^{-1} absorptions without changing the C bands. The new bands reached full intensity after 290-1000-nm photolysis as in Figure 2b; the new 918.0- and 924.0-cm^{-1} doublet had intensities A = 0.04 and 0.12, respectively.

One $CDCl_3$ experiment was performed; the product absorptions at 2059, 1894, 1122, 961, 864, and 798 cm^{-1} are in agreement with previous work.[6,7] On 290-1000-nm photolysis, a strong 472-cm^{-1} and a weaker 924-cm^{-1} absorption appeared while the A absorption counterparts were decreased by 50%.

Important new data from the study of $CHCl_2Br$ are shown in the infrared spectrum of Figure 1b; the original six chloroform product absorptions each have two counterparts, which are also labeled A and C in the figure. Two new broad bands were observed at 2795 and 2681 cm^{-1}, two new sharp bands at 2488 and 2447 cm^{-1}, weak new bands at 1287 and 1254 cm^{-1}, sharp new bands at 1258 and 1245 cm^{-1}, a new triplet at 1048, 1045, and 1042 cm^{-1}, a doublet at 988 and 983 cm^{-1}, and new doublets at 846 and 844 cm^{-1} and 805 and 801 cm^{-1}. In addition, weak 888- and 836-cm^{-1} bands due to the CCl_2Br free radical[13] were observed. The new bands in the $CHCl_2Br$ experiment exhibited interesting photolysis behavior. Exposure of the sample to 420-1000-nm light *decreased* the 2795-, 2488-, 1258-, and 846-, 844-cm^{-1} bands by 33% and *increased* the 2681-, 2447-, 1245-, and 805-, 801-cm^{-1} bands by 33% without changing the other absorptions; further ultraviolet photolysis decreased the intensities of both groups of absorptions, as summarized in Table II.

Two investigations with $CHCl_2I$ produced new sets of product absorptions which are illustrated in Figure 1c and listed in Table III. In the higher frequency region two new broad absorptions and two new weak sharp bands were observed at 2863, 2670, 2470, and 2386 cm^{-1}, respectively, while in the lower frequency region a sharp new band was observed at 1245 cm^{-1}, a new 3:2 relative intensity doublet appeared at 854 and 852 cm^{-1}, and a new 3:1 doublet was found at 797 and 793 cm^{-1}. Also, weak bands were observed at 871 and 810 cm^{-1} which are due to the CCl_2I free radical.[13] On 420-1000-nm photolysis, the 2863-, 2470-, 1245-, and 854-, 852-cm^{-1} bands *decreased* by 50% and the 2670-, 2386-, and 797-, 793-cm^{-1} bands were not changed. Photolysis with ultraviolet light decreased both sets of new absorptions, as seen in Table III.

The $CHCl_2I$ infrared absorptions are of interest as the spectrum of this compound has not been previously reported. The C-H stretching mode at 3055 cm^{-1} is near the 3058-cm^{-1} $CHCl_3$ and 3063-cm^{-1} $CHCl_2Br$ values. The doubly degenerate deformation mode of $CHCl_3$ at 1224 cm^{-1} splits into bands at 1221 and 1181 cm^{-1} for $CHCl_2Br$ and 1216 and 1142 cm^{-1} for $CHCl_2I$. The antisymmetric and symmetric C-Cl_2 stretching modes for $CHCl_2I$ at 759 and 713 cm^{-1} are slightly lower than the 767- and 727-cm^{-1} values for $CHCl_2Br$. The C-I stretching mode of $CHCl_2I$ at 546 cm^{-1} falls below the C-Br mode of $CHCl_2Br$ at 608 cm^{-1}.

Discussion

The new product species will be identified, and the spectroscopic effects of hydrogen bonding will be described for the X^--HCX_2 molecular anion.

Cation. The bands labeled C in the figures were destroyed by 220-1000-nm photolysis while CX_3^+ and CX_3 absorptions were produced; the chloroform C bands have been assigned to $CHCl_2^+$ by JM.[6,7] These absorptions are better characterized

Table I. Absorptions (cm^{-1}) and Intensities (absorbance units) Observed on 15 K Deposition of an Ar/$CHCl_3$ = 400/1 Sample (90% ^{13}C Enriched) during Exposure to Argon Discharge Radiation and Following Filtered High-Pressure Mercury Arc Photolysis[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	assign
697	0.03	sh[b]	sh	0.03	HCl_2^-
705	0.05	1.2	0.33	0.24	$(HCl_2^-)(CCl)$
724	0.03	0.03	0.03	0.04	$^{13}CCl_2$
811.2	0.18	0.06	0.12	0.10	$(Cl^--H^{13}C^{35}Cl^{37}Cl)$
813.5	0.30	0.10	0.20	0.17	$(Cl^--H^{13}C^{35}Cl_2)$
819	0.06	0.06	0.04	0.02	?
836	0.02	0.005	0.010	0.005	$(Cl^--H^{12}C^{35}Cl^{37}Cl)$
838	0.03	0.01	0.015	0.01	$(Cl^--H^{12}C^{35}Cl_2$
867	0.04	0.04	0.04	0.07	$^{13}CCl_3$
870	0.09	0.10	0.10	0.18	$^{13}CCl_3$
874	sh	sh	0.03	0.03	$^{13}CHCl_2$
891.7	0.00	0.03	0.01	0.01	$(HCl_2^-)(^{13}C^{37}Cl)$
898.0	0.005	0.10	0.04	0.03	$(HCl_2^-)(^{13}C^{35}Cl)$
904.5	0.01	0.01	0.02	0.04	Ar_nH^+
924	0.00	0.01	0.00	0.00	$(HCl_2^-)(^{12}C^{35}Cl)$
974	0.005	0.14	0.04	0.03	$(HCl_2^-)(CCl)$
1000.5	0.01	0.01	0.04	0.09	$^{13}CCl_3^+$
1003.5	0.04	0.04	0.12	0.25	$^{13}CCl_3^+$
1007.0	0.08	0.07	0.04	0.02	$(^{13}CH^{37}Cl_2^+)Cl$
1010.0	0.46	0.40	0.25	0.13	$(^{13}CH^{35}Cl^{37}Cl^+)Cl$
1013.0	0.68	0.60	0.40	0.20	$(^{13}CH^{35}Cl_2^+)Cl$
1016.9	0.025	0.03	0.03	0.03	$^{13}CH^{35}Cl^{37}Cl^+$
1019.8	0.04	0.05	0.05	0.05	$^{13}CH^{35}Cl_2^+$
1035.4	0.04	0.03	0.015	0.01	$(^{12}CH^{35}Cl^{37}Cl^+)Cl$
1038.3	0.07	0.06	0.04	0.02	$(^{12}CH^{35}Cl_2^+)Cl$
1268.0	0.16	0.06	0.10	0.07	$(Cl^--H^{13}CCl_2)$
1271.0	0.015				$(Cl^--H^{12}CCl_2)$
1282	0.06	0.06	0.04	0.02	$(^{13}CHCl_2+)Cl$
1291	0.007	0.007			$(^{12}CHCl_2^+)Cl$
2493.0	0.35	0.13	0.22	0.18	$(Cl^--H^{13}CCl_2)$
2499.0	0.04	0.01	0.02	0.02	$(Cl^--H^{12}CCl_2)$
2714	0.26	0.10	0.17	0.14	$(Cl^--H^{13}CCl_2)$
2723	sh	sh	sh	sh	$(Cl^--H^{12}CCl_2)$
3047.8	0.22	0.22	0.22	0.22	$^{13}CHCl_3$
3058.3	0.02	0.02	0.02	0.02	$^{12}CHCl_3$

[a] $h\nu_1$ is 30 min of 290-1000-nm photolysis, $h\nu_2$ is 30 min of 220-1000-nm photolysis, $h\nu_3$ is 100 min of additional 220-1000-nm photolysis.
[b] sh denotes unresolved shoulder.

as $(CHCl_2^+)Cl$ since CX_3^+ and CX_3 appear on photolysis, and the $(CHCl_2^+)Cl$ species displays 4-10-cm^{-1} shifts from $(CHCl_2^+)Br$, generated from $CHCl_2Br$, and from isolated $(CHCl_2^+)$ prepared from methylene chloride.[14] These positive ions will be discussed in more detail when complete spectroscopic and photochemical data on the products formed from the bromine substituted compounds $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ and their deuterium isotopes are presented in a separate report.[9]

Mechanism of Formation. A brief explanation of the mechanism of formation of charged species in these experiments is in order. The positive ions are produced by argon resonance (11.6-11.8 eV) photoionization of $CHCl_3$ during matrix condensation,[8,10] a process requiring 11.5 eV.[15]

$$CHCl_3 + h\nu\,(11.6\text{-}11.8\text{ eV}) \rightarrow (CHCl_2^+)Cl + e^- \quad (1)$$

Reaction 1 shows the chlorine atom byproduct trapped in the same matrix cage with the $CHCl_2^+$ ion. In the analgous $CHCl_2Br$ experiments, the triplet cation absorption displaced 10 cm^{-1} demonstrates a bromine effect on the absorbing species and identifies the cation product as $(CHCl_2^+)Br$. The $CHCl_2I$ studies, however, failed to produce a strong cation absorption; a weak 1045- and 1042-cm^{-1} doublet in this experiment is probably due to isolated $(CHCl_2^+)$.[14] The major photoionization process with $CHCl_2I$ probably gives $CHCl_2$ and I^+; the former radical, detected at 902 cm^{-1},[16] is expected to be a weaker absorber than the analogous cation. A competing photoionization reaction may produce $(CHClI^+Cl$, tentatively identified by photosensitive 869- and 570-cm^{-1} absorptions.

Many of the electrons produced in reaction 1 are captured by chloroform molecules, the most abundant electron trap in the matrix. The parent radical anion, probably produced first, subsequently eliminates a chloride ion to form the $HCCl_2$ radical.

$$CHCl_3 + e^- \rightarrow [CHCl_3^-] \rightarrow Cl^- + HCCl_2 \rightarrow Cl^-\text{-}HCCl_2 \quad (2)$$

The matrix, however, entraps the Cl^- and $HCCl_2$ products together and allows rearrangement to the more stable hydrogen-bonded structure Cl^--$HCCl_2$, which is the subject of the following discussion.

Anion. The chloroform product bands labeled A at 2723, 2499, 1271, and 838 cm^{-1} were simultaneously decreased by 340-600- and 290-1000-nm photolysis, and were first increased and then decreased by prolonged 220-1000-nm photolysis, which indicates that they are probably due to the same molecular species. This set of bands was also observed by JM with the same relative intensities after photolysis of $CHCl_3$ matrix samples containing sodium atoms, and was assigned to the $CHCl_2^-$ anion.[6] The bands labeled A in the present experiments are thus due to the same chloroform-electron capture product studied by JM; however, the new spectroscopic data demonstrate the presence of a third inequivalent halogen atom in the product anion and provide a basis for its reassignment to Cl^--$HCCl_2$, an intramolecular hydrogen-bonded chloroform anion.

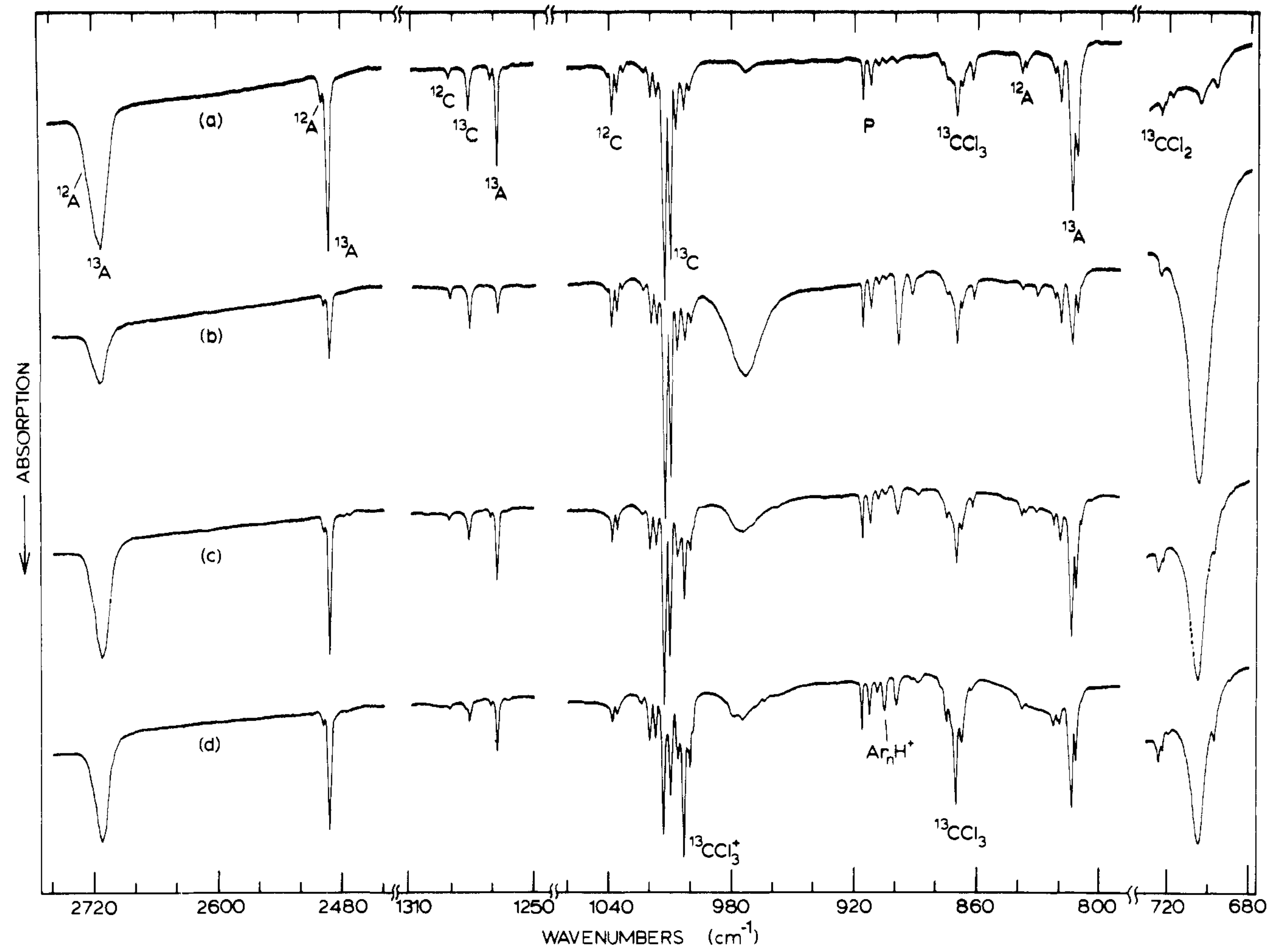

Figure 2. Expanded-scale infrared spectrum of an Ar/^{13}CHCl$_3$ = 400/1 matrix sample (90% ^{13}C) codeposited with simultaneous argon resonance photoionization for 20 h (trace (a)). Scan (b) followed 30 min of 290-1000-nm photolysis; and (c) was recorded after 30 min of 220-1000-nm photolysis; the final trace (d) followed an additional 100 min of full arc 220-1000-nm irradiation.

Infrared spectra from the $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ experiments[9] show that the chloroform A bands have *six* mixed chlorobromo counterparts. This is most clearly described for the sharp 2499-cm^{-1} $CHCl_3$ product band, which has 2488- and 2447-cm^{-1} counterparts with $CHCl_2Br$, 2435- and 2397-cm^{-1} analogues with $CHClBr_2$, and a single sharp 2383-cm^{-1} component with $ClHBr_3$. These mixed chlorobromo spectra thus exhibited three "pairs" of bands, 2499-2488, 2447-2435, and 2397-2383 cm^{-1}, which show a major dependence on two equivalent halogen atoms and a minor dependence on a third inequivalent halogen atom.

Further supporting evidence is found by comparison of the $CHCl_3$, $CHCl_2Br$, and $CHCl_2I$ product spectra. The natural chlorine isotopic splittings on the 838-cm^{-1} $CHCl_3$ product band[6] and on the 846-cm^{-1} $CHCl_2Br$ and 854-cm^{-1} $CHCl_2I$ product bands also characterize this vibration as a mode involving two equivalent chlorine atoms. The 8-cm^{-1} differences between precursors, however, indicate a small dependence on a third halogen atom. Also, the broad 2723-cm^{-1} $CHCl_3$ product band is replaced by two broad bands at 2795 and 2681 cm^{-1} in the $CHCl_2Br$ experiments and by two broad 2863- and 2670-cm^{-1} bands in the $CHCl_2I$ studies. Two new product bands show that either a Br^- or Cl^- ion may be formed in the electron capture process with the chlorobromo precursor, and that either an I^- or Cl^- ion may be produced by electron capture of $CHCl_2I$.

The carbon-13 and deuterium isotopic shifts and the bromine and iodine substitution data for the 2723-, 2499-, 1271-, and 838-cm^{-1} $CHCl_3$ product absorptions strongly support the Cl^--$HCCl_2$ identification of the product anion with the following vibrational assignments: the broad 2723-cm^{-1} band is due to the C-H stretching mode of the hydrogen-bonded species, ν_s; the sharp 1271-cm^{-1} band is the hydrogen bending mode, ν_b; the sharp 2499-cm^{-1} absorption is due to its overtone, $2\nu_b$; and the strong 838-cm^{-1} absorption is due to the antisymmetric C-Cl$_2$ stretching mode, ν_x. Vibrational assignments for the three X^--$HCCl_2$ anions and the Cl^--$HCClBr$ and Cl^--$HCClI$ species are given in Table IV. The ν_b mode for Cl^--$HCClI$ is predicted at 1214 cm^{-1}, under a strong precursor absorption; however, a 1210-cm^{-1} shoulder on this precursor band exhibited the proper photolysis behavior and it could be the ν_b absorption of Cl^--$HCClI$.

The strong broad (15-cm^{-1} full width at half-maximum) band at 2723 cm^{-1} exhibits the characteristics of a hydrogen-bonded C-H vibration, ν_s.[5] Although the C-H stretching mode for the $HCCl_2$ radical has not been observed, this frequency is probably near the $CHCl_3$ value and a 3058 ± 100 cm^{-1} estimate is reasonable, since the hydrogen deformation mode of the $HCCl_2$ radical at 1226 cm^{-1} [16] is in close agreement with the $HCCl_3$ frequency at 1225 cm^{-1}. Hydrogen bonding increases the intensity and bandwidth, and shifts a C-H stretching absorption by 10% to *lower* frequency, precisely the effect observed for the 2723-cm^{-1} absorption. The (C-H)/(C-D) stretching frequency ratio for the chloroform product bands is 2723/2059 = 1.3225, which is slightly smaller than the ratio for $CHCl_3$ and $CDCl_3$, 3058/2278 = 1.3424.

Table II. Absorptions (cm^{-1}) and Intensities (absorbance units) Observed in an Argon Discharge Experiment with Bromodichloromethane

abs	I_0	$h\nu_1$[a]	$h\nu_2$	$h\nu_3$	$h\nu_4$	assign
801	0.02	0.02	0.01	0.01		$(Cl^{-}-HC^{37}ClBr)$
805	0.06	0.07	0.03	0.03	0.01	$(Cl^{-}-HC^{35}ClBr)$
822	0.10	0.10	0.10	0.10	0.08	$CHCl_2Br$
836	0.02	0.02	0.02	0.02	0.09	CCl_2Br
844	0.10	0.07	0.04	0.04	0.01	$(Br^{-}-HC^{35}Cl^{37}Cl)$
846	0.15	0.10	0.06	0.06	0.02	$(Br^{-}-HC^{35}Cl_2)$
886	0.01	0.01	0.01	0.01	0.06	$C^{35}Cl^{37}ClBr$
888	0.02	0.02	0.02	0.02	0.09	$C^{35}Cl_2Br$
904	0.00	0.00	0.00	0.00	0.06	Ar_nH^+
954	0.01	0.01	0.01	0.04	0.10	CCl_2Br^+
983	0.05	0.05	0.05	0.08	0.01	$(CH^{37}ClBr^+)Cl$
988	0.16	0.16	0.16	0.27	0.04	$(CH^{35}ClBr^+)Cl$
993	0.00	0.00	0.00	0.03	0.00	site
1018	0.00	0.00	0.00	0.01	0.06	$C^{35}Cl^{37}ClBr^+$
1020	0.01	0.01	0.01	0.03	0.09	$C^{35}Cl_2Br^+$
1042	0.015	0.02	0.03	0.06	0.05	$(CH^{37}Cl_2^+)Br$
1045	0.10	0.12	0.10	0.12	0.09	$(CH^{35}Cl^{37}Cl^+)Br$
1048	0.14	0.17	0.10	0.08	0.05	$(CH^{35}Cl_2^+)Br$
1245	0.09	0.11	0.05	0.04	0.02	$(Cl^{-}-HCClBr)$
1254	0.01	0.01	0.01	0.015	0.00	$(CHClBr^+)Cl$
1258	0.12	0.080	0.050	0.040	0.02	$(Br^{-}-HCCl_2)$
1287	0.04	0.04	0.02	0.00	0.00	$(CHCl_2^+)Br$
1292	0.03	0.03	0.02	0.02	0.01	$CHCl_2^+$
2447	0.15	0.20	0.08	0.06	0.03	$(Cl^{-}-HCClBr)$
2488	0.12	0.08	0.04	0.04	0.015	$(Br^{-}-HCCl_2)$
2681	0.15	0.19	0.10	0.08	0.03	$(Cl^{-}-HCClBr)$
2795	0.20	0.14	0.07	0.07	0.04	$(Br^{-}-HCCl_2)$
3063	0.30	0.30	0.30	0.30	0.30	$CHCl_2Br$

[a] $h\nu_1$ is 420–1000 nm, $h\nu_2$ is 340–600 nm, $h\nu_3$ is 290–1000 nm, and $h\nu_4$ is 220–1000 nm high-pressure mercury arc photolysis.

Table III. Absorptions (cm^{-1}) and Intensities (absorbance units) Observed on 15 K Condensation of $Ar/CHCl_2I$ = 400/1 Samples with Simultaneous Exposure to Argon Discharge Radiation and after Filtered Mercury Arc Photolysis[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	assign
570	0.02	0.00	0.00	0.00	$(CHClI^+)Cl$
793	0.015	0.015	0.00	0.00	$(Cl^{-}-HC^{37}ClI)$
798	0.05	0.05	0.01	0.00	$(Cl^{-}-HC^{35}ClI)$
811	0.015	0.015	0.015	0.02	CCl_2I
838	0.05	0.05	0.05	0.05	?
852	0.03	0.01	0.01	0.00	$(I^{-}-HC^{35}Cl^{37}Cl)$
854	0.04	0.015	0.015	0.005	$(I^{-}-HC^{35}Cl_2)$
869	0.05	0.00	0.00	0.00	$(CHClI^+)Cl$
871	0.03	0.03	0.03	0.04	CCl_2I
902	0.02	0.02	0.02	0.03	$CHCl_2$
1042	0.012	0.012	0.012	0.005	$CH^{35}Cl^{37}Cl^+$
1045	0.02	0.02	0.02	0.01	$CH^{35}Cl_2^+$
1245	0.04	0.015	0.015	0.005	$(I^{-}-HCCl_2)$
1284	0.03	0.03	0.03	0.03	?
2386	0.02	0.02	0.00	0.00	$(Cl^{-}-HCClI)$
2470	0.02	0.01	0.01	0.00	$(I^{-}-HCCl_2)$
2670	0.10	0.10	0.03	0.00	$(Cl^{-}-HCClI)$
2863	0.06	0.03	0.02	0.005	$(I^{-}-HCCl_2)$
3055	0.30	0.30	0.30	0.30	$CHCl_2I$

[a] $h\nu_1$ is 30 min of 420–1000-nm photolysis, $h\nu_2$ is 30 min of 290–1000-nm photolysis, and $h\nu_3$ is 30 min of 220–1000-nm photolysis.

This is consistent with a larger cubic anharmonic term in the hydrogen-bonded C–H vibrational potential function. The carbon-13 shift, from 2723 to 2714 cm^{-1}, is precisely that expected for a C–H stretching mode, since the C–H stretching mode of $CHCl_3$ at 3058 cm^{-1} exhibited a carbon-13 shift of 10.5 cm^{-1}. The C–H stretching mode was red shifted to 2863 cm^{-1} for $I^{-}-HCCl_2$, to 2795 cm^{-1} for $Br^{-}-HCCl_2$, and to 2723 cm^{-1} for $Cl^{-}-HCCl_2$; the smaller red shifts for the iodide and bromide hydrogen-bonded C–H modes are in accord with the progressively weaker hydrogen bonding expected for the larger halide ions with decreasing proton affinities.

It is interesting to note that the fluoride compound in this series has a significantly stronger hydrogen bond, and this species is more correctly written as $(F-H---CCl_2)^-$, based on infrared spectroscopic studies.[17] The $Cl^{-}-HCCl_2$, $Br^{-}-HCCl_2$, and $I^{-}-HCCl_2$ anions are classified as type I hydrogen bonding[18] species, and the increase in C–H stretching frequency with the heavier halide (weaker hydrogen bond) is clearly characteristic of the B···H–A system. The larger proton affinity of fluoride ion, however, produces more proton transfer, and the fluoride compound in this series probably involves a type III hydrogen bond.[17b]

The intensity of the C–H stretching mode for $Cl^{-}-HCCl_2$ is markedly stronger than this mode for $CHCl_3$. The absorbance of the 3058-cm^{-1} mode of $CHCl_3$ in solid argon is 2% of the 767-cm^{-1} antisymmetric $C-Cl_3$ stretching mode; however,

Table IV. Vibrational Assignments (cm^{-1}) to the X^--HCX_2 Intramolecular Hydrogen-Bonded Anions

	Cl^--$HCCl_2$	Cl^--$H^{13}CCl_2$
ν_s	2723	2714
$2\nu_b$	2499	2493
ν_b	1271	1268
ν_x	838	813
	Br^--$HCCl_2$	Cl^--$HCClBr$
ν_s	2795	2681
$2\nu_b$	2488	2447
ν_b	1258	1245
ν_x	846	805
	I^--$HCCl_2$	Cl^--$HCClI$
ν_s	2863	2670
$2\nu_b$	2470	2386
ν_b	1245	[a]
ν_x	854	797

[a] Estimated at 1214 cm^{-1} under the intense $CHCl_2I$ absorption.

the absorbances of the 2723- and 838-cm^{-1} bands of Cl^--$HCCl_2$ are comparable, and if integrated intensities are considered, the ν_s mode is fivefold more intense than ν_x. Hence, the hydrogen bonding of Cl^- to $HCCl_2$ has probably increased the infrared intensity of the C-H stretching mode by two orders of magnitude.

The sharp, weak 1271-cm^{-1} band has the characteristics of a hydrogen-bonded C-H bending mode, ν_b.[5] Hydrogen bonding decreases the intensity, does not affect the bandwidth, and shifts a C-H bending mode about 3% to ***higher*** frequency, exactly as observed for the 1271-cm^{-1} vibration relative to the 1226-cm^{-1} value for the radical H-CCl_2. The H/D bending frequency ratio for the product bands is 1271/961 = 1.3226, which is also slightly smaller than the parent ratio, 1225/914 = 1.3403. This indicates a larger cubic anharmonic term in the hydrogen-bonded C-H deformation potential function. In addition, the weaker iodide complex I^--$HCCl_2$ only shifted ν_b to 1245 cm^{-1} and the bromide species Br^--$HCCl_2$ displaced the bending mode to 1258 cm^{-1}, whereas the stronger chloride complex shifted this mode a greater amount to 1271 cm^{-1}.

The sharp, stronger 2499-cm^{-1} band is assigned to the first overtone of the 1271-cm^{-1} bending mode. This assignment is in agreement with the carbon-13 shifts of 3.0 ± 0.2 cm^{-1} for ν_b and 6.0 ± 0.2 cm^{-1} for $2\nu_b$. Furthermore, the earlier assignment of the 2499-cm^{-1} band to a C-H stretching mode[6] requires a 7.5-cm^{-1} carbon-13 shift, clearly greater than the 6.0 ± 0.2 cm^{-1} value observed for the 2499-cm^{-} band. The carbon-13 data thus strongly supports the present overtone assignment of the sharp 2499-cm^{-1} band. The greater intensity of $2\nu_b$ compared to ν_b for Cl^--$HCCl_2$ is probably due to large anharmonicity. The mode ν_b is clearly more anharmonic than the analogous ν_4 mode of $CHCl_3$ since 2 × ν_4 of $CHCl_3$ exceeds $2\nu_4$ by only 18 cm^{-1},[19] whereas 2 × ν_b exceeds $2\nu_b$ by 43 cm^{-1} For the less anharmonic deuterium mode in the Cl^--$DCCl_2$ species, $2\nu_b$ is considerably less intense than ν_b, as expected, and 2 × ν_b exceeds $2\nu_b$ by only 28 cm^{-1}. The overtone $2\nu_b$ is clearly more anharmonic than the fundamental ν_b as shown by the overtone H/D ratio 2499/1894 = 1.3194 as compared to the fundamental ratio 1271/961 = 1.3226.

The unusually great intensity of $2\nu_b$ compared to ν_b of Cl^--$HCCl_2$ is not without precedent. When $CHCl_3$ hydrogen bonds to trimethylamine, the $2\nu_4$ mode of $CHCl_3$ is considerably more intense than ν_4.[20] In the complex $Cs^+(HCl_2)^-$, the bending mode overtone is stronger than the fundamental.[21] These effects have been rationalized on the basis of electrical anharmonicity (nonlinear dependence of the electric dipole moment on internuclear distance) which arises from the unusually large charge mobility along the bond axis with a change in internuclear distance.[21] This argument is appropriate for the present ion-molecule Cl^--$HCCl_2$ species.

The mixed chlorobromo and chloroiodo species also provide support for this overtone assignment. For the chloride complex species Cl^--$HCClBr$, 2 × ν_b exceeds $2\nu_b$ by 43 cm^{-1} showing comparable anharmonicity to the Cl^--$HCCl_2$ complex, whereas the bromide complex Br^--$HCCl_2$ has 2 × ν_b greater than $2\nu_b$ by only 28 cm^{-1}, indicating less anharmonicity in the deformation for the weaker hydrogen-bonded bromide complex. In the still weaker I^--$HCCl_2$ complex, 2 × ν_b exceeds $2\nu_b$ by 20 cm^{-1} showing progressively less anharmonicity.

The 838-cm^{-1} band is clearly due to an antisymmetric C-Cl_2 vibration of one carbon and two chlorines, as originally assigned based on carbon-13 and natural chlorine isotopic shifts.[6] This absorption, however, appears intermediate between the analogous HC-Cl_2 radical mode at 902 cm^{-1}, which has a relatively high frequency due to π bonding in the radical,[16] and the C-Cl_2 mode of the completed octet valence species H_2C-Cl_2 at 749 cm^{-1}.[14] The 838-cm^{-1} C-Cl_2 vibration is more appropriate for a perturbed radical than a $CHCl_2^-$ anion with a complete octet of electrons about the central carbon; the latter species would be expected to absorb near or below 750 cm^{-1}. The stronger chloride complex shifts the HC-Cl_2 radical mode from 902 to 838 cm^{-1}, whereas the weaker bromide complex shifts this mode from 902 to 846 cm^{-1}, and the still weaker iodide complex displaces this mode a lesser amount from 902 to 854 cm^{-1}. This reduction in antisymmetric C-Cl_2 frequency upon hydrogen bonding is probably due to a reduction in the π bonding[16,22] responsible for the high 902-cm^{-1} frequency of the $HCCl_2$ radical, since charge transfer from the hydrogen-bonded chloride ion to the $HCCl_2$ free radical increases antibonding electron density in the C-Cl_2 π-bonding system.

Photolysis of the Anion. The molecular anion bands were decreased by 60% upon 290-1000-nm photolysis, as shown in Figure 2b for the isotopic Cl^--$H^{13}CCl_2$ species, while a very intense 705-cm^{-1} band, a broad 974-cm^{-1} absorption, and a comparatively sharp 892-898-cm^{-1} doublet appeared. After photolysis of the Cl^--$H^{12}CCl_2$ species, new unshifted 705- and 974-cm^{-1} bands were produced, but the 1:3 relative intensity doublet shifted to 918 and 924 cm^{-1}; after photolysis of the Cl^--$DCCl_2$ anion, the strong band appeared at 472 cm^{-1}, but the weaker 924-cm^{-1} band was not shifted. Jacox[7] noted the proximity of the broad 705- and 974-cm^{-1} bands to the sharp 697- and 956-cm^{-1} absorptions of isolated HCl_2^- and assigned the former to a perturbed bichloride ion (HCl_2^-) (M) without characterizing M; the present studies reveal the identification and origin of the perturbing species M. The above isotopic data for the sharp 924-cm^{-1} absorption indicate a vibration of one carbon and one chlorine atom and suggest that carbon monochloride radical is the perturbing species. Since the isolated CCl radical absorbs at 866 cm^{-1} in solid argon with 6- and 26-cm^{-1} ^{37}Cl and ^{13}C isotopic shifts,[23] the present characterization of M as the CCl radical is confirmed. Photolysis of the anion product, reaction 3, to give (HCl_2^-) and (CCl) provides further support for the ionic nature and the Cl^- $HCCl_2$ identification of the chloroform electron-capture product.

$$Cl^-\text{-}HCCl_2 + h\nu\ (290\text{-}1000\ \text{nm}) \rightarrow (HCl_2^-)(CCl) \quad (3)$$

Final photolysis with full 220-1000-nm mercury arc light decreased both of these molecular anions. Since the complete chloroform stoichiometry is maintained in these anions and the photodetachment threshold of chloride ion is 343 nm,[24] the final photolysis likely detaches the electron and produces the original $CHCl_3$ molecule.

Conclusions

The identification of the matrix-isolated Cl^{-}-$HCCl_2$ anion invites consideration of the hydrogen-bonded structure and models for hydrogen bonding.

The structure proposed here for the stable chloroform-electron capture product, Cl^{-}- - -H-CCl_2, is an unusual but straightforward intramolecular hydrogen-bonded species, which may help elucidate the bonding interaction between chloride ion and chloroform in the gas phase. Yamdagni and Kebarle[25] have studied the dissociation of the Cl^{-}-$HCCl_3$ complex in a high-pressure mass spectrometer source and proposed a hydrogen-bonded species Cl^{-}- - -H-CCl_3 with a dissociation energy of 15 kcal/mol. The more recent work of Dougherty et al.[26] proposed an association ion with the structure of the S_N2 transiton state. Although the present Cl^{-}-$HCCl_2$ species is not directly applicable to the chloride-chloroform association ion structure, the present work shows that the intramolecular hydrogen-bonded structure is relatively stable and certainly more stable than the chloroform radical anion structure.

The great intensity of ν_s and $2\nu_b$ and the reduced ν_x frequency for Cl^{-}-$HCCl_2$ are all indicative of some charge transfer from chloride to the $HCCl_2$ radical in the hydrogen-bonded species, as has been discussed here. These observations suggest a weak covalent chloride-hydrogen chemical bonding interaction involving electron density from the chloride ion. It has been clearly shown that the halide ion-hydrogen bond strength decreases with decreasing halide ion proton affinity, which is reasonable in view of comparative sizes of the interacting species.

The inert gas matrix is an excellent medium for spectroscopic studies of hydrogen bonding, particularly when ionic systems are being investigated. The matrix provides a pseudo-gas-phase environment allowing spectroscopic data to be obtained without large solvent effects. The bands are sharp, and deuterium, carbon-13 and chlorine-37 isotopic shifts can be determined which provide information on the potential functions for the hydrogen-bonding interaction. As has been demonstrated here, the substitution of an iodide or bromide ion for chloride ion can be used to examine the spectrosopic effect of a weaker hydrogen bond in the same chemical system.

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Cyclization by Radical Displacement on Ester Groups. Conversion of Acetals to Lactones by Radical Abstraction with Stereoelectronic Control of Bond Scission

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Abstract: The thermal reactivities of monoperoxy ester monoester derivatives of diacids were examined. Kinetics and product studies of *tert*-butyl 4-carbomethoxyperbutyrate (**11**), *tert*-butyl *o*-carbomethoxyphenylperacetate (**14**), and *tert*-butyl *o*-carbobenzoxyphenylperacetate (**15**) showed that these materials react by formation of intermediate carbon centered radicals which undergo 4-9% of intramolecular radical attack on the carbonyl oxygen of the ester grouping to give lactones. The intermediate 1-alkoxy-1,4-dihydroisobenzofuran radicals **28** and **29** formed in the reactions of **14** and **15** undergo cleavage of the *O*-alkyl bond exocyclic to the ring in preference to ring opening. This was confirmed by independently generating **28** by hydrogen atom abstraction from 1-methoxy-1,4-dihydroisobenzofuran (**24**), which gave lactone **19** as the major product. A general stereoelectronic explanation is proposed to account for the direction of bond cleavage in **28** and **29**, and for other cases reported in the literature as well.

Radical displacements on carboxyl groups constitute an example of the S_H2 reaction[1] and have been most commonly observed in reactions of percarboxy groups.[2] In every case for which the position of radical attack on acylperoxy groups has been determined by isotope labeling the point of attack has been found to be peroxidic oxygen as shown in eq 1.[1,2] Thus

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