Infrared Spectrum of Dichloroborane Produced by CO_2 Laser Enhanced Reaction

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Infrared spectra of $HBCl_2$ and $DBCl_2$ produced by a TEA CO_2 laser enhanced reaction of BCl_3 and H_2/D_2 have been observed by an FT-IR spectrometer at a resolution of 0.12 cm^{-1}. A detailed analysis has been carried out for the ν_1 band of $HBCl_2$ to obtain the precise molecular parameters, and they are compared with the microwave data. The fundamental frequencies other than the ν_3 band have all been determined. These frequency data combined with the results of an *ab initio* MO calculation have yielded the general symmetry force field through a least squares method. Some characteristic features on the CO_2 laser reaction of BCl_3 and H_2 are also discussed.

Infrared spectra of dichloroborane have been observed by several investigators.[1—7] However, very few analyses of the vibration-rotation bands of this molecule have been reported. Lynds and Bass[6,7] observed the ν_1 and ν_6 bands of dichloroborane with a low resolution using a conventional grating spectrometer, and determined the molecular structure from the observed values of the rotational constants $(A-\bar{B})$.[6] These authors and Dewames[8] calculated the fundamental frequencies of $HBCl_2$ assuming a force field which is similar to that of BCl_3. This was done only to make assignments of the observed bands. Mandirola and Westerkamp also calculated the fundamental frequencies of this molecule assuming appropriate values of the force constants.[9] However, there have been no attempts to determine the force field of this molecule. Quite recently Sugie *et al.*[10] studied the microwave spectra of this molecule. They obtained the rotational constants of $H^{11}B^{35}Cl_2$, $H^{10}B^{35}Cl_2$, $H^{11}B^{35}Cl^{37}Cl$, and $D^{11}B^{35}Cl_2$, and determined the precise structural parameters.

In Ref. 1—7, $HBCl_2$ was produced by heating a mixture of BCl_3 and H_2 in the presence of catalysts, where various compounds such as B_2H_6, B_2H_5Cl, *etc.* besides $HBCl_2$ and HCl were produced. Recently this reaction has been investigated by the use of CO_2 laser photolysis since the strong degenerate stretching band of BCl_3 coincides with a laser band of CO_2.[11—16] Rockwood and Hudson[16] found that the reaction of BCl_3 with H_2 by the irradiation of pulsed CO_2 laser yields only $HBCl_2$ and HCl as final products, the fact being in contrast with the case of thermal reaction. They also found that the efficiency of the reaction is as high as 122 (10.6 μ) photons per $HBCl_2$ molecule.

The purpose of the present study is to observe the vibration-rotation bands of $HBCl_2$ and $DBCl_2$ with relatively high resolution to determine the spectroscopic constants. The study also aims to determine the molecular force field from the observed frequency data. An *ab initio* MO method was used to calculate the force constants, which compensated the insufficient observed data. In connection with the preparation of sample, a CO_2 laser enhanced reaction between BCl_3 and H_2 was investigated.

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Experimental

H_2 and D_2 gases were purchased from Showa Denko Co. and BCl_3 gas from Takachiho Chemical Co. These samples were used without further purification. The BCl_3/H_2 and BCl_3/D_2 gas mixtures were irradiated with a CO_2 laser beam in a glass reaction vessel of 13 cm in length and 3.2 cm in diameter fitted with KBr windows. Grease was not used in the vacuum sampling system to avoid contamination. A Pirani vacuum gauge and an MKS Baratron capacitance manometer were used to measure the pressures. A Lumonics model TEA-101-2 pulsed CO_2 laser was used to irradiate the sample. Burn patterns were made in thermal paper to check the distribution of the laser radiation. The laser power was measured with a Lumonics model 20D pyroelectric detector. The laser power was changed by placing an infrared absorption cell filled with an appropriate amount of BCl_3 gas before the reaction cell. The reaction was monitored by the absorbance of infrared spectrum taken after the irradiation with the laser shots.

The vibration-rotation spectra were measured with a Nicolet 7199 FT-IR spectrometer equipped with a Ge coated KBr beam splitter and a water cooled Glober source. All the spectra were observed at a resolution of 0.12 cm^{-1}. Since no attempt was made to separate and purify the sample of $HBCl_2$, absorption bands of BCl_3 and HCl/DCl were also observed.

Results and Discussion

Observed Spectra. Since the ν_1, ν_2, and ν_3 modes belong to A_1 species, they should give B-type bands. The ν_1 band which is associated with the B–H stretching mode showed a symmetrical band contour as shown in Fig. 1. In a prolate symmetric top approximation, the frequencies of the Q branch peaks are given by

$$\nu_0^{\rm sub} = \nu_0 + (1\pm 2K)(A'-\bar{B}') + \{(A'-A'')-(\bar{B}'-\bar{B}'')\}K^2 \mp D_{\rm k}(2K^2\mp 2K+1)(2K+1), \quad (1)$$

where the single and double primes refer to the upper and lower states, respectively. $D_{\rm k}$ is a centrifugal distortion constant. $\bar{B}$ is an average of B and C rotational constants. The observed frequencies of $H^{11}BCl_2$ were

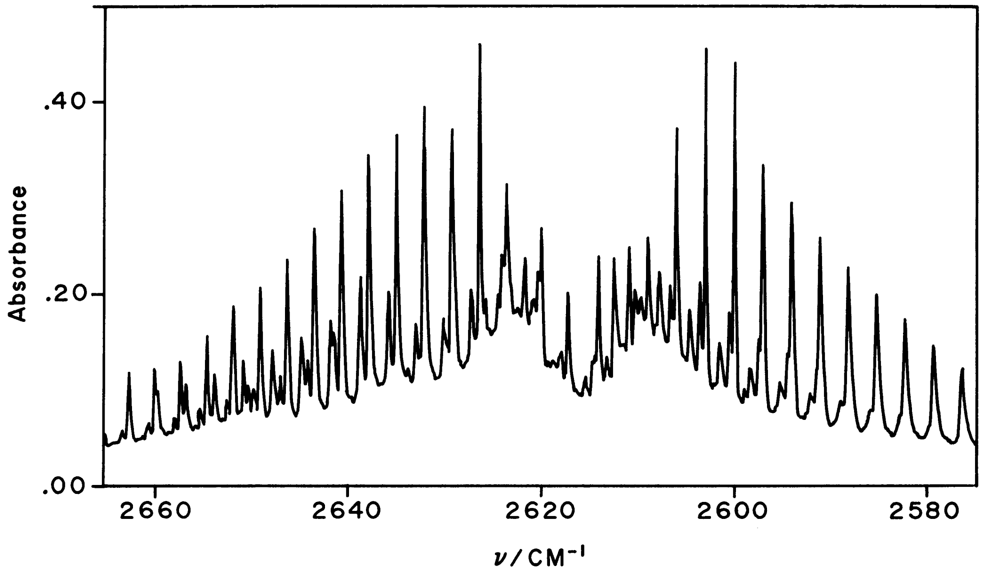

Fig. 1. Spectrum of ν_1 band of $H^{11}BCl_2$.

used for a least squares method by using Eq. 1 leading to the following;

$$\nu_1^{sub} = 2616.25 + 1.4580(1 \pm 2K) - 0.00352(K^2) \mp 0.0000479(2K^2 \mp 2K + 1)(2K+1). \quad (2)$$

Since the band center area is overlapped by the hot bands as well as by the absorption of various isotopic species, the lines of small K values were not included in the calculation. Thus, the band center of ν_1 was determined as 2616.25 cm^{-1} for ^{11}B species. For ^{10}B species, the assignment was made so that the resulting values of the rotational constants agree well with the microwave values,[10] and the band center was determined as 2628.00 cm^{-1}. No assignment was made for the hot bands. The resulting values of the spectroscopic constants for this band are summarized in Table 1. The rotational constants are in good agreement with the microwave values shown in Table 2.[10] This fact con-

Table 1. Analysis of the ν_1 band of $HBCl_2$. (cm^{-1})

$K^{a)}$	$H^{11}B^{35}Cl_2$		$H^{10}B^{35}Cl_2$	
	Obsd	O–C	Obsd	O–C
3	2626.421	−0.003		
4	2629.312	0.006	2641.780	0.003
5	2632.165	−0.001	2644.791	−0.002
6	2635.038	0.005	2647.788	−0.003
7	2637.878	0.003	2650.778	0.006
8	2640.701	0.000	2653.729	−0.004
9	2643.500	−0.010	2656.675	0.001
10	2646.299	−0.003		
11	2649.068	−0.007		
12	2651.851	0.024		
13	2654.559	0.001		
14	2657.258	−0.009		
15	2659.949	−0.001		
−5	2603.094	0.025		
−6	2600.115	−0.016	2610.960	−0.001
−7	2597.191	−0.001	2607.865	0.012
−8	2594.245	−0.010	2604.728	−0.006
−9	2591.319	0.000	2601.624	0.011
−10	2588.392	0.006	2598.487	−0.007
−11	2585.456	−0.002		
−12	2582.536	0.001		
ν_0	2616.258(21)		2628.003(12)	
$A'-\bar{B}'$	1.4580(15)		1.5382(16)	
$(A'-A'')-(\bar{B}'-\bar{B}'')$	−0.00352(25)		−0.00506(30)	
D_K	0.0000479(57)		0.000051(11)	
$A''-\bar{B}''$	1.46152		1.54326	
$A''-\bar{B}''^{b)}$	1.46194		1.54155	

a) Negative K numbers are for P-branch transitions. b) Ref. 10.

TABLE 2. THE ROTATIONAL CONSTANTS OF $HBCl_2$ IN THE GROUND VIBRATIONAL STATE[a)] (cm^{-1})

	$H^{11}B^{35}Cl_2$	$H^{10}B^{35}Cl_2$	$D^{11}B^{35}Cl_2$
A''	1.5647846(23)	1.6445345(27)	1.1725796(23)
B''	0.1062708(3)	0.1062568(3)	0.1062738(3)
C''	0.0994171(3)	0.0997143(13)	0.0973419(3)
$A''-\bar{B}''$	1.461940(2)	1.541549(4)	1.070772(2)

a) Ref. 10.

firms that the observed ν_1 spectrum is definitely due to $HBCl_2$ molecule.

The ν_2 band is due to the symmetric BCl stretching mode. The band center was determined as 734.62 cm^{-1} for $H^{11}B^{35}Cl_2$ species from the analysis of the vibration-rotation band, while for $H^{10}BCl_2$ species, assignment was not made, because the band center area was disturbed by the ν_4 band in addition to the hot bands. The ν_3 band, which is expected to be in the far-ir region, could not be detected.

The out-of-plane bending mode of this molecule gives a C-type band ν_4. For this band each rotational fine structure was observed as a doublet due to isotopic species of $HB^{35}Cl^{37}Cl$ whose abundance is *ca.* two thirds of $HB^{35}Cl_2$. The band centers were determined as 785.92 and 785.73 cm^{-1} for $H^{11}B^{35}Cl_2$ and $H^{11}B^{35}Cl^{37}Cl$, respectively. For ^{10}B species, the band center was determined only for $H^{10}B^{35}Cl_2$ species as 798.70 cm^{-1}.

The B_2 vibrational modes give A-type bands, which have a similar appearance to that of a parallel band of symmetric top molecule. The ν_5 B–Cl asymmetric stretching band was found at 1091.1 cm^{-1} for $H^{11}BCl_2$ and 1108.0 cm^{-1} for $H^{10}BCl_2$. The B–H in-plane deformation band, ν_6, was observed at 895.4 cm^{-1} for $H^{11}BCl_2$ and 916.5 cm^{-1} for $H^{10}BCl_2$. The ν_5 and ν_6 bands have conspicuously strong intensities compared with the other bands. The ν_6 band center area of $H^{11}BCl_2$ was slightly different in its shape from that of ν_5. From this fact, a large difference of the rotational constant A between the upper and lower states of ν_6 is expected. The observed frequency data for $HBCl_2$ are summarized in Table 3.

For $DBCl_2$ molecule, two bands were observed with about equal intensities in the BD streching band region. This is because the ν_1 and $2\nu_5$ bands are in Fermi resonance with each other. A slightly stronger one was tentatively assigned to the ν_1 band. Thus, the ν_1 band center for $D^{11}BCl_2$ was determined as 1979.94 cm^{-1}. This band is strongly disturbed also by the DCl rotation-vibration lines and by the hot bands. The ν_2 band center of $D^{11}BCl_2$ is completely obscured by the ν_6 band. The ν_3 band which is expected to be in the far-ir region could not be detected for $DBCl_2$, either.

The band center of the out-of-plane mode, ν_4, was found to be 647.21 cm^{-1} for $D^{11}BCl_2$ and 662.60 cm^{-1} for $D^{10}BCl_2$. As shown in Fig. 2, the splittings due to $DB^{35}Cl^{37}Cl$ species were also observed and its band center was determined as 646.99 cm^{-1}.

The B–Cl asymmetric stretching band, ν_5, was found at 975.20 cm^{-1} for $D^{11}BCl_2$. However, the band region for $D^{10}BCl_2$ was heavily overlapped by the ν_3 band of BCl_3, and we could not observe the band shape clearly. The B–D in-plane deformation band, ν_6, of $D^{11}BCl_2$ located at about 723 cm^{-1} is disturbed by the ν_2 band. Therefore, it was difficult to determine the band center precisely; the value given above is an approximate one. The observed date of $DBCl_2$ are also summarized in Table 3.

Force Constants. A normal coordiate calculation was carried out by the convensional GF method developed by Wilson *et al.*[17] In Fig. 3, the internal coordinates of $HBCl_2$ are illustrated. The out-of-plane coordinate, γ, is the angle between the BH bond and the ClBCl plane. The symmetry coordinates are given in terms of the internal coordinates as listed in Table 4. The adjustment of force constants was

TABLE 3. THE OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF DICHLOROBORANE (cm^{-1})

Mode			$H^{11}B^{35}Cl_2$	$H^{10}B^{35}Cl_2$	$D^{11}B^{35}Cl_2$	$D^{10}B^{35}Cl_2$
A_1	ν_1	Obsd.[a)]	2616.25	2628.00	1979.94	—
		Fitted[b)]	2622.6	2634.0	1938.4	1955.5
		Calcd.[c)]	2866.1	2878.4	2117.2	2135.6
	ν_2	Obsd.	734.62	—	—	—
		Fitted	735.0	757.4	712.4	731.1
		Calcd.	777.2	801.2	753.9	773.9
	ν_3	Obsd.	—	—	—	—
		Fitted	285.8	287.7	283.9	285.8
		Calcd.	316.8	318.9	314.7	316.8
B_1	ν_4	Obsd.	785.92	798.70	647.21	662.60
		Fitted	786.0	799.0	646.7	662.5
		Calcd.	863.6	877.9	710.1	727.3
B_2	ν_5	Obsd.	1091.11	1107.96	975.20	—
		Fitted	1091.4	1108.6	974.1	1012.4
		Calcd.	1234.1	1248.8	1057.8	1097.4
	ν_6	Obsd.	895.35	916.50	723.0	—
		Fitted	895.5	917.5	721.5	722.6
		Calcd.	960.7	988.0	805.8	808.5

a) Observed value. b) Calculated with the determined force constants listed in Table 5. c) *Ab initio* value.

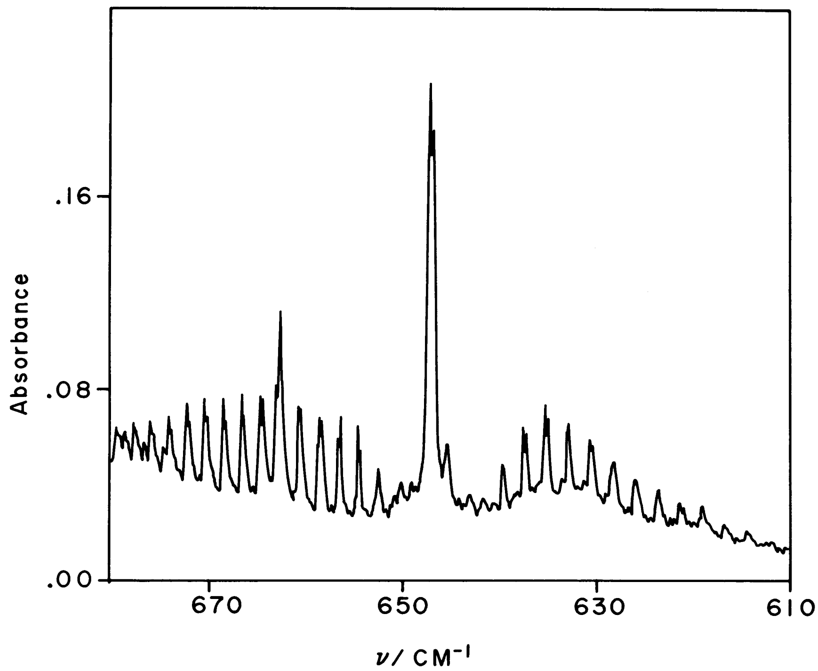

Fig. 2. Spectrum of ν_4 band of $D^{11}BCl_2$.

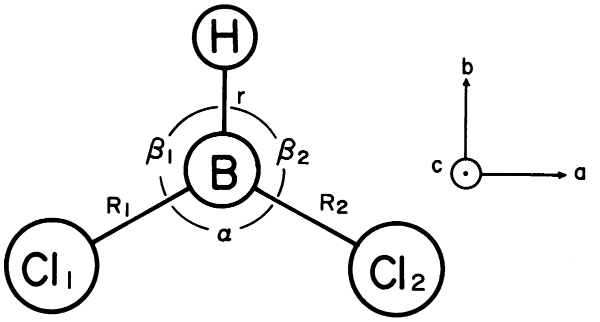

Fig. 3. Internal coordinates of $HBCl_2$ molecule.

TABLE 4. SYMMETRY COORDINATES FOR $HBCl_2$ MOLECULE

Species	Band type	Symmetry coordinate	Mode
A_1	B	$S_1=\Delta r$	B-H str
		$S_2=(\Delta R_1+\Delta R_2)/\sqrt{2}$	B-Cl sym-str
		$S_3=(2\Delta\alpha-\Delta\beta_1-\Delta\beta_2)/\sqrt{6}$	B-Cl sym-def
B_1	C	$S_4=\Delta\gamma$	out-of-plane
B_2	A	$S_5=(\Delta R_1-\Delta R_2)/\sqrt{2}$	B-Cl antisym-str
		$S_6=(\Delta\beta_1-\Delta\beta_2)/\sqrt{2}$	B-H def

made by using a standard least squares method such as developed by Shimanouchi *et al.*,[18] where, in each repeating cycle of the refinement procedure, the corrections to the force constants, $\Delta \boldsymbol{P}$, were made by solving the following normal equation;

$$\boldsymbol{J'WJ}\Delta\boldsymbol{P}=\boldsymbol{J'W}\Delta\boldsymbol{\nu} \quad (3)$$

where $\boldsymbol{J}$ denotes the Jacobian matrix, $\boldsymbol{W}$ the weight vector for the observed frequencies, and $\Delta\boldsymbol{\nu}$ the frequency error vector.

For B_1 and B_2 species, the number of the data was enough to determine all force constants uniquely and the results of the least-squares calculation are shown in Table 5. However, for A_1 species the number of the data was not enough to determine all six force constants uniquely. Then, in order to make predictions of the harmonic force field, an *ab initio* MO calculation was carried out. The calculation was made with the Pople's 4-31G* basis set by using the HONDOG computer program.[19] After geometry optimization was carried out by the gradient method,[20] the harmonic force field $\boldsymbol{F}_x$ was calculated. The $\boldsymbol{F}_x$ was transformed to a symmetry coordinates expression to give the $\boldsymbol{F}_s$ matrix. The harmonc force field of $HBCl_2$ thus obtained is shown in the second column of Table 5. These force constants were found to reproduce the observed fundamental frequencies fairly well as is clearly seen in Table 3. The agreement is markedly improved if the calculated frequencies are multiplied by an arbitrary factor of 0.9. This means that a factor of 0.81 should be used for the calculated force constants to fit them to the observed. Therefore, in order to determine the force constants for A_1 block from the

TABLE 5. QUADRATIC FORCE CONSTANTS OF $HBCl_2$ (mdyne/Å or rad)

	Determined	*ab initio*
F_{11}	3.747(42)	4.518
F_{12}	0.084[a)]	0.104
F_{13}	−0.076[a)]	−0.094
F_{22}	4.214(172)	4.665
F_{23}	0.160[a)]	0.197
F_{33}	0.647[a)]	0.799
F_{44}	0.448(8)	0.538
F_{55}	3.265(71)	3.721
F_{56}	0.256(21)	0.312
F_{66}	0.428(11)	0.553

a) Constrained.

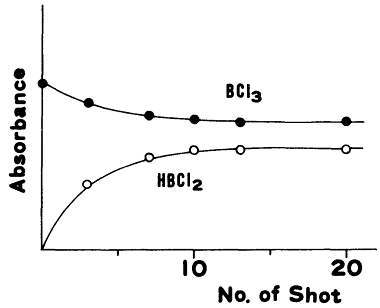

Fig. 4. Relation between the spectral intensities and number of laser shots for BCl_3 and $HBCl_2$.

observed frequencies, the values of F_{12}, F_{13}, F_{23}, and F_{33} were constrained to the *ab initio* values multiplied by a factor of 0.81. The resulting values of the force constants are listed in Table 5. The calculated values of the fundamental frequencies from these force constants are also compared with the observed in Table 3.

CO_2 Laser Reaction of BCl_3 with H_2. As to the laser induced reaction used in the present study, a few characteristic features were noticed. For example, when the partial pressure of BCl_3 was less than 1 Torr†, we did not observe any appreciable changes in the infrared spectrum of the sample even after the 1000 shots of laser irradiation with fluence of 1.27 J/cm²/pulse, *i.e.* neither any absorption due to $HBCl_2$ nor any appreciable intensity change in BCl_3 bands was observed. However, the reaction did take place when the laser power density was increased by focusing the beam with an optical lens. When the sample pressures were raised to 5 Torr of BCl_3 and 5 Torr of H_2, the reaction became very rapid and it reached equilibrium after only 10 laser shots as shown in Fig. 4. This means that the threshold laser fluence for the reaction of BCl_3 with H_2 strongly depends on the pressure of BCl_3. It is concluded from this experiment that the average number of photons absorbed per molecule per pulse also depends on the pressure of the sample. This conclusion is demonstrated in Fig. 5, where non-linear dependence of the laser absorption on the BCl_3 sample pressure is clearly shown. The plotted data were obtained by taking the ratios of the laser power measured before and after the laser beam passes through the sample cell. In Fig. 5, the result of similar measurements for SiF_4 gas by P(42) CO_2 laser line is also shown for comparison. In both cases, non-linearity of the relationship between the absorbance and gas pressure is clearly demonstrated. Since almost the same absorption coefficients are obtained for the different laser fluences, the non-linearity may not be caused by the largeness of laser power. The most likely explanation of this phenomenon is that the pressure broadening of the BCl_3 absorption line is necessary to absorb the CO_2 laser efficiently. The very low absorption coefficient of the laser at low pressure probably causes the existence of the power threshold for the laser induced reaction between BCl_3 and H_2. The fact that the equilibrium mixture of BCl_3 and $BHCl_2$ is obtained as shown in Fig. 4 suggests that this reaction is almost thermal.

† 1 Torr ≈ 133.322 Pa.

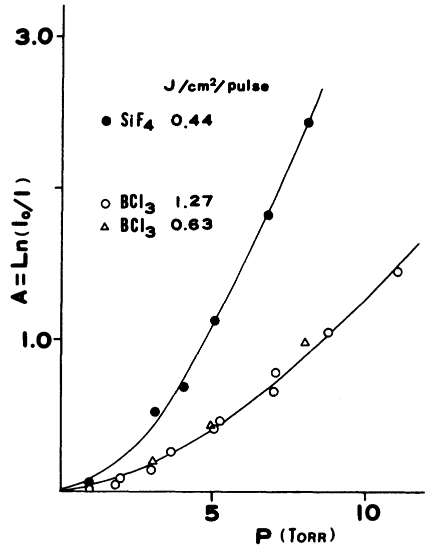

Fig. 5. Non-linear relationship between the absorbance and partial pressure for laser beam absorption by BCl_3 and SiF_4.

As described previously, the laser induced reaction between BCl_3 and H_2 does not produce B_2H_5Cl, although the external heating does. One reason may be that the catalyst is not used in the laser reaction and, therefore, the reaction occurs purely in the gas phase. Another possible reason is that the reaction products are cooled very rapidly in the pulsed laser reaction. This frozens the high temperature state so that the byproduct such as B_2H_5Cl which is not stable at elevated temperatures cannot be produced.

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