Determination of the *Gauche* Dihedral Angle and the Energy Difference between Rotational Isomers of Bromoacetyl Chloride

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Infrared absorption intensities of fundamental bands of bromoacetyl chloride were measured in carbon disulfide solution, an absolute intensity method being applied to determine the energy difference between the rotational isomers. In order to determine the dihedral angle of the less stable isomer, normal frequencies and band intensities were calculated for various angles, the results being compared with observed data. The dihedral angle of the *gauche* isomer was found to be 100° which is in good agreement with the angle in chloroacetyl chloride. The energy difference, 0.91 kcal/mol, determined in carbon disulfide solution is in good agreement with the value obtained by the temperature variation method.

The dihedral angle of the *gauche* isomer of chloroacetyl chloride $CH_2ClCOCl$ was determined to be 105°, by calculating normal frequencies and infrared band intensities for both isomers and comparing the results with observed data.$^{1)}$ The dihedral angle herewith denotes the angle between C–Cl of CH_2Cl and C=O of COCl, the angles of the *trans* and *cis* isomers being 0 and 180°, respectively. However, 105° for the dihedral angle of the less stable form was in some disagreement with results obtained by the other authors.

Nakagawa *et al.*$^{2-4)}$ obtained 150° by calculating normal frequencies for skeletal vibrations, while Khan and Jonathan$^{5)}$ obtained 180°. On the other hand, Bellamy and Williams$^{6)}$ concluded that the *gauche* dihedral angle is 120°, by considering a polar effect on carbonyl frequencies; and Le Fèvre *et al.*$^{7)}$ obtained 120° by dipole moment analysis.

It is known that, in rotational isomers with a C–C bond as an internal rotational axis, double bonds such as C=C or C=O bonds are apt to take a *cis* position with a single bond on the opposite side. It thus seems reasonable that the *gauche* isomer of haloacetyl halide takes a dihedral angle of 120°, although the dihedral angle of the less stable isomer of CH_2FCOF was determined to be 180° by microwave spectroscopy,$^{8)}$ the isomer taking a *cis* form. In the case of $CH_2ClCOCl$, owing to repulsive interaction between the two chlorine atoms in a molecule, the dihedral angle of the *gauche* isomer might decrease from 120 to 105°.

In order to support the result for the *gauche* dihedral angle obtained previously, bromoacetyl chloride molecule was treated by the same method as before. The energy difference between the rotational isomers was determined by applying the absolute intensity method.$^{1,9)}$

Experimental

The infrared absorption spectrum of $CH_2BrCOCl$ was observed in a carbon disulfide solution with a Perkin-Elmer Model 180 grating spectrophotometer combined with a digital recorder. The spectrum is shown in Fig. 1. Observed frequencies were calibrated by referring to standard gas spectra$^{10)}$ within an accuracy of 1 cm^{-1}.

Absorption band intensities were evaluated, by means of a FACOM Model 270-30 electronic computer system by processing encoded paper tapes punched out from the digital recorder. Concentration of solutions was 0.05—0.3 (mol/l), thickness of sealed liquid cells with KBr windows being 0.1—1.0 mm. Absorption intensities were evaluated by averaging intensities obtained for at least ten measurements in various concentrations for individual bands. For absorption bands below 400 cm^{-1}, sealed liquid cells with polyethylene windows were used, the absorption intensities being roughly estimated with a planimeter. Other experimental condifions for the intensity measurement were the same as described previously.$^{1,9,11-15)}$

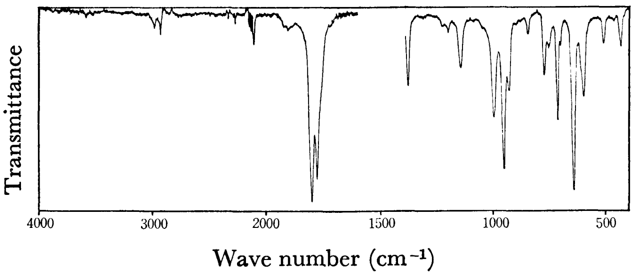

Fig. 1. The infrared absorption spectrum of $CH_2BrCOCl$ observed in carbon disulfide solution.

A Hitachi Model IRH-3 high temperature cell, in combination with a Hitachi Model IRC-2 power regulator, was used for determination of energy difference by the temperature variation method. The temperature of the cell was controlled within 1 °C.

Results and Discussion

In order to determine the dihedral angle of the less stable isomer of $CH_2BrCOCl$, normal frequencies of both isomers were calculated for various angles 60—180°. Force constants based on the local symmetry force field (LSFF) were assumed to take the same values between the rotational isomers. Their values were determined by the least squares method so as to attain the best fit between the calculated and observed frequencies. Since Nakagawa *et al.*$^{2-4)}$ made assignments for only skeletal vibrations, fundamental frequencies were determined by referring to their assignment and to those of $CH_2ClCOCl$ and $CH_2BrCOBr$.$^{1)}$

First the refinement of all the twenty-four force constants was attempted by means of the observed twenty-eight frequency data. Some of the force constants converged showing relatively large standard deviations. Thus three force constants were fixed, and

Table 1. Observed and calculated frequencies of $CH_2BrCOCl$ for various dihedral angles of the less stable isomer (cm^{-1})

Species	i	ν_{obsd}	ν_{calcd} for the dihedral angel of					
			60°	90°	150°	120°	150°	180°
trans A′	1	2946	2947	2947	2947	2947	2946	2946
	2	1812	1798	1800	1803	1804	1799	1797
	3	1388	1399	1399	1399	1398	1397	1394
	4	1237	1227	1226	1226	1227	1233	1235
	5	968	963	967	966	964	969	973
	6	728	724	730	729	726	729	736
	7	658	653	652	652	651	649	647
	8	443	456	438	440	451	469	469
	9	252	263	257	257	258	264	270
	10	181	168	170	169	174	181	189
trans A″	11	2999	2997	2997	2997	2997	2999	2999
	12	1156	1158	1159	1159	1159	1157	1156
	13	944	938	939	939	938	914	898
	14	473	470	472	471	471	473	475
	15	—	97	87	93	90	75	60
gauche A	1	2999	3001	3001	3001	3001	3000	2999
	2	2946	2945	2945	2945	2945	2946	2946
	3	1789	1800	1802	1805	1808	1804	1800
	4	1409	1398	1398	1398	1399	1401	1403
	5	1210	1220	1221	1221	1220	1213	1211
	6	1156	1153	1152	1152	1153	1155	1156
	7	1011	1019	1026	1022	1016	1001	1007
	8	855	858	847	854	865	898	901
	9	713	718	713	711	714	713	711
	10	612	620	617	618	618	615	612
	11	520	526	525	511	500	492	491
	12	473	457	462	469	473	473	470
	13	348	337	353	354	351	333	324
	14	157	169	167	165	163	149	137
	15	—	82	69	74	73	70	63

Table 2. Converged values and standard deviations of LSFF force constants (Unit: mdyn/Å, mdyn, or mdyn·Å)

LSFF	60°	105°	150°
f(as)	4.78(0.01)	4.78(0.01)	4.79(0.01)
f(ss)	4.86(0.03)	4.86(0.01)	4.86(0.02)
f(CO)	10.70(1.54)	10.71(0.58)	10.69(4.23)
f(sc)	0.47(0.34)	0.47(0.08)	0.47(0.29)
f(wa)	0.53(0.12)	0.53(0.06)	0.49(0.11)
f(tw)	0.61(0.00)	0.61(0.01)	0.61(0.00)
f(CC)	3.50[a)]	3.50[a)]	3.50[a)]
f(ro)	0.78(0.02)	0.79(0.02)	0.75(0.09)
f(CCl)	2.78[a)]	2.78[a)]	2.78[a)]
f(CBr)	2.66[a)]	2.66[a)]	2.66[a)]
f(π)	0.30(0.01)	0.30(0.01)	0.31(0.02)
f(CCO)	1.13(1.16)	1.06(0.54)	1.22(0.52)
f(CCCl)	2.02(0.52)	2.00(0.50)	2.02(3.52)
f(CCBr)	0.86(0.30)	0.88(0.21)	1.03(0.33)
f(to)	0.15(0.03)	0.14(0.36)	0.09(0.06)
f(sc, CC)	0.24(1.54)	0.23(0.37)	0.22(1.19)
f(wa, CC)	0.14(1.04)	0.14(0.36)	−0.02(0.65)
f(CC, CBr)	0.19(1.35)	0.19(0.35)	0.24(1.07)
f(CC, CCO)	0.83(1.06)	0.86(0.52)	0.81(1.50)
f(CC, CCCl)	0.29(1.45)	0.26(0.52)	0.35(1.02)
f(CC, CCBr)	0.16(2.03)	0.16(0.71)	0.13(1.06)
f(CCl, CCO)	0.08(0.73)	0.17(0.25)	0.06(0.77)
f(CCl, CCCl)	−0.30(0.75)	−0.35(0.46)	−0.36(1.31)
f(CBr, CCrB)	0.45(0.69)	0.43(0.33)	0.37(1.99)

ss: CH_2 symmetric stretching, as: CH_2 antisymmetric stretching, sc: CH_2 scissoring, wa: CH_2 wagging, tw: CH_2 twisting, ro: CH_2 rocking, π: out-of-plane beinding, to: torsion. a) Fixed force constants.

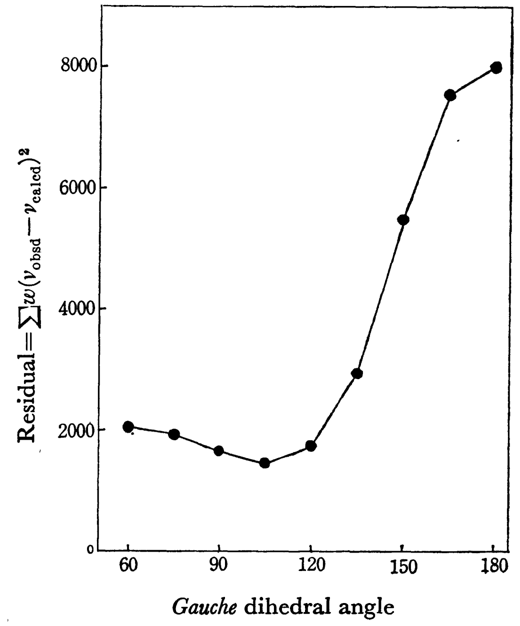

Fig. 2. The plot of residuals against various assumed *gauche* dihedral angles.

the other force constants adjusted by the least-squares method. The calculated frequencies and the LSFF force constants with their standard deviations in parentheses are given in Tables 1 and 2, respectively.

The converged values of the force constants show no dependence on the *gauche* dihedral angle, while the calculated normal frequencies show remarkable dependence on the dihedral angle assumed for the less stable isomer. The calculated frequencies for the *trans* ν_{10}, *gauche* ν_{12} bands are in poorer agreement with the observed frequencies, as the dihedral angle of the *gauche* isomer approaches 60°. On the other hand, those for the *trans* ν_8, ν_9, ν_{13}, *gauche* ν_8, ν_{11}, ν_{13}, ν_{14} bands are in poorer agreement as the dihedral angle of the less stable isomer approaches 180° (*cis* form).

In order to examine the agreement more quantitatively, the weighted sum of squared deviations or the residual was computed and plotted against the assumed dihedral angle of the less stable isomer (Fig. 2). The result indicates that the most probable *gauche* dihedral angle is between 90 and 120°. For the angle 150° determined by Nakagawa *et al.*, the residual is much larger than those for angles 90—120°, and their result is not consistent with ours.

For the sake of confirmation, infrared band intensities were computed for various angles assumed for the *gauche* isomer. For intensity parameters, electro-optical parameters based on Gribov's valence-optical theory[16,17] were taken, and their values determined by the least squares method. In order to determine the

Table 3. Convergd values and standard deviations of intensity parameters for the *gauche* dihedral angles of 60°, 105°, 150°
(Unit: D/Å, or D)

	60°	105°	150°
μ_{CH}	0.64(0.07)	0.70(0.06)	0.44(0.07)
μ_{CO}	−1.93(0.22)	−1.17(0.21)	−1.04(0.17)
μ_{CCl}	−1.16(0.43)	−1.21(0.32)	−2.14(0.26)
μ_{CBr}	−1.69(0.44)	−1.47(0.27)	−2.15(0.35)
$\delta\mu_{CH}/\delta r_{CH}$	0.59(0.05)	0.58(0.05)	0.60(0.05)
$\delta\mu_{CH}/\delta r_{CH'}$	0.23(0.05)	0.22(0.05)	0.23(0.04)
$\delta\mu_{CH}/\delta\alpha_{HCH}$	0.33(0.08)	0.43(0.07)	0.31(0.07)
$\delta\mu_{CH}/\delta\alpha_{HCBr}$	0.00(0.08)	0.08(0.09)	0.05(0.09)
$\delta\mu_{CH}/\delta\alpha_{HCC}$	−0.71(0.07)	−0.66(0.08)	−0.58(0.07)
$\delta\mu_{CO}/\delta r_{CO}$	−7.11(0.20)	−6.76(0.20)	−6.18(0.19)
$\delta\mu_{CO}/\delta\alpha_{CCO}$	−2.07(0.20)	−1.71(0.17)	−1.71(0.21)
$\delta\mu_{CCl}/\delta r_{CCl}$	−2.52(0.56)	−2.90(0.21)	−3.41(0.47)
$\delta\mu_{CCl}/\delta\alpha_{CCCl}$	−1.86(0.36)	−1.43(0.33)	−0.07(0.44)
$\delta\mu_{CBr}/\delta r_{CBr}$	−3.09(0.39)	−3.19(0.27)	−2.64(0.35)
$\delta\mu_{CBr}/\delta\alpha_{CCBr}$	2.41(0.30)	2.98(0.29)	2.29(0.45)
X	0.68(0.01)	0.70(0.01)	0.67(0.01)

population ratio of the rotational isomers, the absolute intensity method was applied. Converged values and standard deviations of intensity parameters and of the *trans* population ratio parameter are given in Table 3. Calculated band intensities are given in Table 4 together with observed intensities for comparison.

As in the normal frequency calculation, the converged values of the intensity parameters show no dependence on the *gauche* dihedral angle, while the calculated intensities depend remarkably on the *gauche* dihedral angle. The calculated intensities for the 1156, 348 cm^{-1} bands are in poorer agreement with the observed values as the dihedral angle approaches 60°, while those for the 658, 612 cm^{-1} bands are in poorer agreement as the dihedral angle approaches 180°. The plot of residuals against the assumed *gauche* dihedral angles is

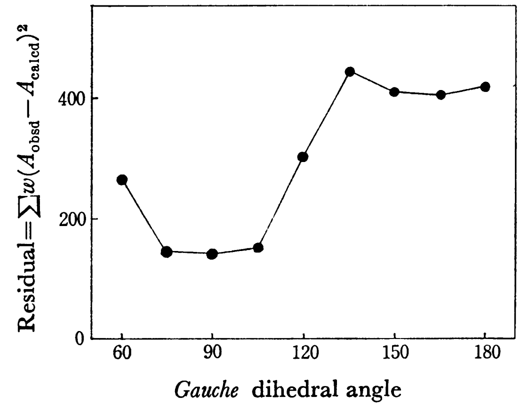

Fig. 3. The plot of residuals against various assumed *gauche* dihedral angles.

Table 4. Observed and calculated infrared intensities for various dihedral angles of the less stable isomer (Unit: l mol$^{-1}\cdot$cm^{-2})

ν_{trans}	ν_{gauche}	A_{obsd} (Error)	A_{calcd} for the dihedral angle of 60°	90°	105°	120°	150°	180°
2999		900 (50)	721	744	725	693	569	539
	2999		192	164	180	198	265	278
2946		950 (50)	656	670	676	694	664	652
	2946		370	343	334	312	381	399
1812		12500 (500)	12310	12076	12213	13073	13567	13792
	1789	7900 (300)	7854	7980	7816	7232	7214	7148
	1409	2600 (100)	598	485	471	440	453	485
1388			1857	2262	2324	2314	2135	2103
1237		980 (50)	921	889	878	861	809	837
	1210		317	243	226	179	342	341
1156		2300 (100)	2005	2031	2017	1983	1551	1414
	1156		625	474	498	517	661	725
	1011	10000 (500)	1585	1092	1073	1141	2177	2486
968			5623	5241	4558	4168	3946	3604
944			2259	2081	1931	1726	996	1064
	855	500 (30)	594	373	430	548	587	559
728		2900 (150)	2894	2749	3031	3354	2702	2265
	713		760	716	1210	1735	1789	1722
658		8700 (400)	8965	9182	9008	7877	3621	2869
	612	3600 (200)	3245	1847	1671	1404	1022	1047
	520	880 (30)	309	871	769	420	570	694
473		200 (20)	577	186	176	223	482	555
	473		686	741	797	719	424	293
443		990 (50)	737	1067	966	924	1483	1398
	348	300 (50)	771	902	779	575	236	93
252		100 (40)	44	78	61	45	22	23
180		300 (100)	344	411	423	411	339	298
	157	—	293	256	261	239	176	63

given in Fig. 3. This also indicates that the most probable dihedral angle of the less stable isomer is between 75 and 105°.

Taking into account the results from normal frequency calculation and intensity computation at the same time it can be concluded that the dihedral angle of the *gauche* isomer of $CH_2BrCOCl$ is 100±10°. This is in line with the angle 105° obtained for $CH_2ClCOCl$.[1]

Nakagawa *et al.*[2] calculated normal frequencies for skeletal vibrations using UBFF force constants derived from related molecules, and concluded that the *gauche* form is considered to have a dihedral angle of 150°. However, the calculated normal frequencies for vibrational modes other than skeletal vibrations are also affected considerably by the assumed *gauche* dihedral angle (Table 1).

The *gauche* isomer of the haloacetyl halide molecule seems to take a dihedral angle of about 120°. However, if we take into account the repulsive force between the halogen atoms in molecule, the dihedral angle might become smaller than 120°. The angle 150° obtained by Nakagawa *et al.* indicates that the two carbon-halogen bonds approach each other from eclipsed configuration between the C–H and C=O bonds. Such an approach does not seem acceptable; the angle 150° is unconvincing.

The angle we obtained is in good accordance with the concept stated above, and might be more reasonable as the *gauche* dihedral angle of $CH_2BrCOCl$.

The energy difference between the *trans* and *gauche* isomers has been evaluated by the same method as before[1] from the converged value of the *trans* population ratio parameter X (Table 3). The entropy term is estimated from principal moments of inertia and fundamental frequencies for both isomers by the equation

$$\exp\left(\frac{\Delta S}{R}\right) = 2\frac{(I_aI_bI_c)_G^{1/2}\Pi(1-e^{-h\nu_G/kT})^{-1}}{(I_aI_bI_c)_T^{1/2}\Pi(1-e^{-h\nu_T/kT})^{-1}}$$

From the values of this entropy term and of the *trans* population ratio parameter, the energy difference ΔE is evaluated by

$$\frac{1-X}{X} = \exp\left(-\frac{\Delta E}{RT}\right)\cdot\exp\left(\frac{\Delta S}{R}\right)$$

The value 0.91±0.10 (kcal/mol) is thus obtained (Table 5).

In order to confirm the validity of this value, the energy difference was also determined by the temperature variation method. Absorption intensities for the *trans* ν_8 (at 443 cm^{-1}) and *gauche* ν_{11} (at 520 cm^{-1}) bands were measured in a carbon disulfide solution with a high temperature cell in the temperature range 25—100 °C. Although the boiling point of carbon disulfide is 46 °C and its vapor pressure reaches about 5 atm at 100 °C, the experiment could be carried out at 100 °C owing to the air-tightness of the cell.

TABLE 5. ENERGY DIFFERENCES OF HALOACETYL HALIDE MOLECULES (kcal/mol)

Molecule	Vapor	CS_2 solution
$CH_2ClCOCl$	0.97[5]	1.39[1]
$CH_2BrCOCl$	1.0[2]	0.91[a]
$CH_2BrCOBr$	1.9[2]	0.97[1]

a) This study.

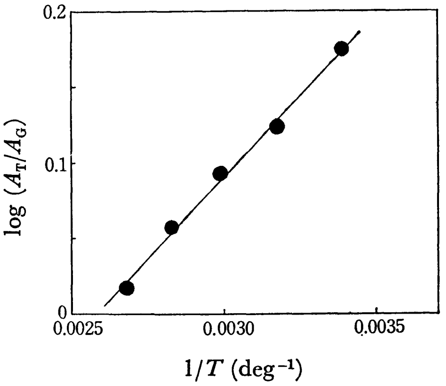

Fig. 4. The van't Hoff plot for determining the energy difference.

The van't Hoff plot for determining the energy difference is given in Fig. 4. From the slope of the least squares fitted straight line, the energy difference of $CH_2BrCOCl$ in carbon disulfide solution was obtained as 0.99±0.10 (kcal/mol). This is in good agreement with the value determined by the absolute intensity method and with the value 1.0 (kcal/mol) obtained by Nakagawa *et al.*

It is of interest to note that in $CH_2ClCOCl$, the energy difference in the vapor phase is smaller than in carbon disulfide solution; in $CH_2BrCOBr$, the former is about twice larger than the latter, and that the situation in $CH_2BrCOCl$ is intermediate between in $CH_2ClCOCl$ and $CH_2BrCOBr$ (Table 5).

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