Studies on Molecular Structure by the Measurement of the Dielectric Constant of Gases. II. Dipole Moment and the Molecular Structure of Mono- and sym-Dihalogenomethyl ether

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In halogenomethyl ether, CH_3OCH_2X, the two groups CH_3O–and CH_2X–have the possibility of rotating around the central C–O bond. The rotation around C–C bond has been extensively studied hitherto, but the rotation about C–O bond has not been so often subjected to examination. In addition, the group CH_3O– has a dipole moment opposite in its direction to that of the group –CH_2X, i.e. the dipole of the former group points towards the oxygen atom, while that of the latter points outward from the central carbon to the halogen atom. This situation is not encountered in the case of dihalogenoethanes. The problem has already been investigated by the measurement of dipole moment in non-polar solution[1], Raman effect[2], and infrared absorption spectrum[3]. The conclusion obtained is that the molecule has a shallow minimum about the equilibrium position so that there exists a wide distribution of molecules from the equilibrium position. The present work is carried out on mono and di-halogenomethyl ethers to investigate the molecular structure in the gaseous state from the standpoint of the dipole moment at various temperatures, for a slight change in the molecular configuration may sensibly be detected by the dipole moment measurement.

Preparation of the Materials

Monochloromethyl Ether CH_2ClOCH_3 was synthesized[4] from methanol, formalin, and hydro-

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[1] Y. Morino, H. Shiio and I. Miyagawa, *Repts. Radiation Chem. Research Inst.* (Tokyo Univ.), 5, 6 (1950).

[2] M. Katayama and Y. Morino, ibid., 4, 1, (1949).

[3] S. Mizushima, T. Shimanouchi, T. Miyazawa and M. Hayashi, unpublished.

[4] *Org. Synthesis*, vol. 9, p. 59.

gen chloride. Dry air was passed through the crude distilate to exile the dissolved hydrogen chloride and then redistilled, b.p. 55–57°C.

***sym*-Dichloromethyl Ether** CH_2ClOCH_2Cl was synthesized[5] by the reaction of chlorosulfonic acid on polyoxymethylene in conc. sulfuric acid. It was purified as above, b.p. 103°C.

Monobromomethyl Ether CH_2BrOCH_3 was synthesized[6] from polyoxymethylene, methanol, and hydrogen bromide. It was purified as above, and redistilled, b.p. 86–88°C.

***sym*-Dibromomethyl Ether** CH_2BrOCH_2Br was synthesized[7] from polyoxymethylene, red phosphorus, and bromine, b.p. 148–150°C.

Experimental Procedure and Results

The apparatus for the measurement of dielectric constant was reported in the preceding paper[8]. The compounds are all reactive, and particularly, decompose readily in moist air. For monochloro- and monobromo-methyl ether, the usual gas filling method cannot be used on account of their low boiling point. The sample is first introduced in a trap which is connected to the cell, cooled with dry ice during the evacuation of the apparatus, and then evaporated to fill the gas cell by bringing the trap to room temperature. This operation has the disadvantage that the vapor contacts the grease of the cocks.

In the case of monobromoether, the observed polarization increases gradually with the runs of observation, so that the temperature dependence of the moment of this substance is also measured in heptane solution. For dibromoether, the measurement is carried out only in heptane solution because of the instability of this compound. The results of the measurements are summarized in Table I[9].

TABLE I

OBSERVED POLARIZATIONS AND DIPOLE MOMENTS OF MONOCHLORO-, DICHLORO-, MONOBROMO-, AND DIBROMO-METHYL ETHERS

Monochloromethyl ether

$MR_D=18.0$ cc. $P_E+P_A=18.9$ cc.

T(°K)	n	p(mm Hg)	P(cc.)	ΔP(cc.)	μ(D)
296.3	6	70–102	82.5	0.6	1.76
337.8	5	83–120	75.1	0.3	1.77
370.4	7	70–103	73.3	0.5	1.82
412.3	7	92–113	68.3	0.4	1.83
467.2	7	81–110	66.2	0.4	1.90

n: number of the observations.

p: pressure range of the observations.

ΔP: average deviations of P.

sym-Dichloromethyl ether

$MR_D=22.9$ cc. $P_E+P_A=24.0$ cc.

T	n	p	P	ΔP	μ
338.3	8	48–82	41.4	0.5	0.98
353.0	8	59–76	40.2	0.5	0.97
371.0	7	54–79	40.7	0.4	1.01
412.2	6	62–83	41.6	0.3	1.09
412.5	5	60–82	41.8	0.6	1.10

Monobromomethyl ether*

$MR_D=20.8$ cc. $P_E+P_A=21.8$ cc.

T	n	p	P	μ
301.0	7	49–68	106.3–106.5	2.04
338.4	5	51–61	95.2– 98.0	2.03–2.07
338.4	8	61–70	93.5– 94.2	2.00
371.0	6	50–60	89.2– 94.0	2.03–2.10
371.1	6	63–74	89.2– 92.5	2.03–2.08
412.0	9	51–67	82.6– 83.4	2.03–2.08

* Observed polarization changes considerably with the runs of observation, so ΔP is not given in this case.

In heptane solution

T	ε_1	d_1(g./cc.)	α	β	$P_{2\infty}$(cc.)	μ
267	1.9574	0.7076	3.38	0.477	128.2	2.16
298	1.9111	0.6810	2.92	0.458	119.1	2.18
330	1.8648	0.6530	2.43	0.399	109.8	2.18

sym-Dibromomethyl ether

$MR_D=28.6$ cc. $P_E+P_A=30.0$ cc.

T	ε_1'**	d_1'**	α	β	$P_{2\infty}$	μ
261	1.971	0.707	5.58	0.506	50.5	0.94
274	1.944	0.697	5.45	0.507	50.9	0.97
297	1.909	0.678	5.16	0.487	50.2	0.99
323	1.874	0.656	4.87	0.460	51.2	1.06

** The prime indicates that these values are extrapolated ones, which differ a little from the values of the pure solvent.

The observed moments of the monochloroether are in good agreement with the values previously reported by Morino, Shiio and Miyagawa in carbon tetrachloride solution[1]. Whereas for dichloroether the discrepancy between the present data and theirs seems fairly large. In the solution method some doubts may exist in the extrapolation to infinite dilution. Indeed, from their data polarization of about 44 cc. is estimated by a more reasonable extrapolation. This is close to the value obtained in the present observation.

Discussion of Results

I) Monochloromethyl Ether.—The result shows a great increase in the moment with temperature. This means that these molecules are a mixture of molecular form of stable, less polar ones and less stable, more polar ones[10]. From the appropriate bond

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[5] H. Stephen, et al., *J. Chem. Soc.*, **117**, 514 (1920).

[6] Karvonen, *Chem. Zentl.*, **1912** II, 1268.

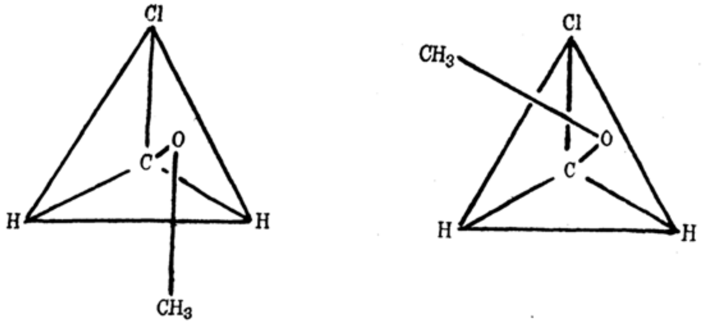
[7] W. Tischtschenko, et al., *Chem. Zentl.*, **1915** I, 837.

[8] T. Chiba, This Bulletin, **28**, 19 (1955).

[9] In the calculation of the moment all the P_E+P_A's are assumed to be 1.05 MR_D.

[10] If a single form is assumed for this molecule, from the observed P *vs.* $1/T$ curve, the moment and the atomic polarization of 1.46 D and 20 cc. is obtained. The latter value is unreasonably high for the molecule of this kind, consequently the assumption of one rigid form is completely denied.

moments and bond angles, the moment of the molecule corresponding to the form in which the CH_3 group and Cl atom are in the *cis* position is calculated to be 0.65D, that of the form in which Cl atom is turned from the *cis* position through 60° (*gauche*) is 1.48D and that of the form in which the two are in the *trans* is 2.74D[11] (Fig. 1). The *cis* position is regarded as quite unstable, since at this position the distance between the Cl atom and the CH_3 group is very short. So we can safely ignore the *cis* form.



trans *gauche*

Fig. 1. The *trans* and *gauche* forms of monochloromethyl ether

From the results of the infrared and Raman effect spectroscopy[2,3], the existence of definite isomers is not concluded but rather the molecule should be distributed over a wide range of the angle of internal rotation. On the other hand, from the numerical calculation of the potential energy of these molecules as a function of the internal rotational angle by the use of appropriate interatomic potential[12], it was found that the molecule has a shallow potential minimum about the *gauche* position in good accord with the results of the spectra. From the temperature dependence of the dipole moment it cannot be decided whether the potential curve, as a function of the internal rotation angle, has minima at the *trans* and the *gauche* position, or whether it increases monotonously from the *gauche* position to the *trans* one: in other words, in such a curve as *a* or *b* in Fig. 2, the polarization vs. $1/T$ curve may be nearly the same in the temperature range of the present experiment. This means that, even if the potential be of the type *b*, the mean dipole moment may be treated by assuming the potential *a*[13]. Therefore, if we assume tentatively that the molecule is composed of the two isomers, *trans* and *gauche*, then from the observed change of the moment with temperature the energy difference of the two forms, ΔE, that is, the energy of the *trans* form minus the energy of the *gauche* one, is found to be approximately 700 cal./mol.[14].

With the model in which bond dipoles are located at the middle point of bond radius, the electrostatic energy between the two bond dipoles OCH_3 and CCl which stabilized the *gauche* position against the *trans* is calculated to be 1.3 kcal./mol.[15], so the observed result suggests that the *trans* position is stabilized by 1.3-0.7=0.6 kcal. due to the steric repul-

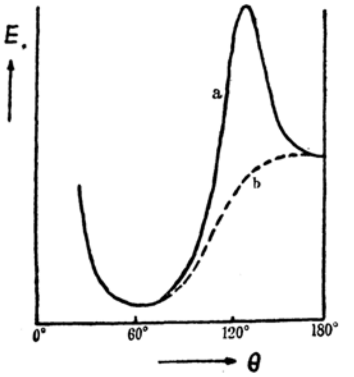


Fig. 2. Two types of intramolecular potential giving, respectively, (a) two separated isomers, and (b) continuous distribution.

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[11] In the calculation the following values of bond moments are assumed: $\mu_{CCl}=1.8$ D, $\mu_{CO}=1.0$ D, $\mu_{CH_3O}=1.1$ D.

[12] H. Shiio, unpublished.

[13] Strictly speaking, this is not true, but the above consideration may be allowed by taking average moment values in the neighborhood of the *trans* and the *gauche* as μ_t and μ_g. To discuss whether the potential be *a* or *b*, needs more precise molecular parameters, which in this case are unfortunately not known.

[14] For the method of estimating ΔE from the observed temperature dependence of the moment, see I. Miyagawa, *J. Chem. Soc. Japan*, (*Pure Chem. Sect.*) 75, 970 (1954).

[15] Assumed bond distances and the bond radii are as follows:

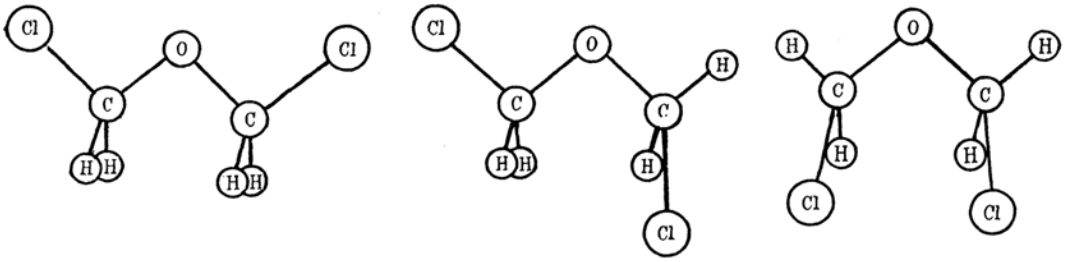
$r_{CCl}=1.76$Å, $r_{CO}=1.42$Å, $r_{C\cdot}=0.77$Å, $r_{O\cdot}=0.65$Å.

sion between CH_3 group and Cl atom. Of course, we cannot put too much significance on the individual figures, because the approximation used here is rather crude, but this is a reasonable magnitude when compared with those of haloethane derivatives. It must now be added that if we assume a mixture of *cis* and *trans* or of *cis*, *gauche* and *trans*, instead of *gauche* and *trans*, the moment of the *trans* form must be considerably higher than the calculated one in order to explain the observed data. This account confirms the validity of the neglection of the *cis* form.

II) *sym*-Dichloromethyl Ether.—Extending the consideration I), the following three forms are assumed: *t,t*-form in which the two chlorine atoms are in the *trans* to the opposite $-CH_2Cl$ group, *t,g*-form in which the one is in the *trans* and the other in the *gauche*, and *g,g*-form in which both are in the *gauche* position[16] (Fig. 3). Using the observed energy difference between the *trans* and the *gauche* forms of monochloro ether in I), the following relations can be obtained, provided that the interatomic distance and valence angles are the same in the two compounds.

$$E_{tt}-E_{gg}=0.7\,\text{kcal.}\times 2+E_{tt}(\mu)-E_{gg}(\mu)$$
$$E_{tg}-E_{gg}=0.7\,\text{kcal.}+E_{tg}(\mu)-E_{gg}(\mu)$$

where E's are the energies corresponding to the individual forms, $E(\mu)$'s are the energies of the dipole interaction of two CCl bond dipoles. Calculating in the same way as in I), $E(\mu)$'s are as follows: $E_{tg}(\mu)-E_{gg}(\mu)=0.5$ kcal., and $E_{tt}(\mu)-E_{gg}(\mu)=1.3$ kcal., leading to the total energy difference of $E_{tg}-E_{gg}=1.2$ kcal. and $E_{tt}-E_{gg}=2.7$ kcal. Therefore, if these arguments are valid, the contribution of *t,t*-form to the observed moment may be neglected. Further, the moment value of *g,g*-form is definitely small, so if it is tentatively assumed to be zero, the observed temperature dependence of the moment gives the values of $E_{tg}-E_{gg}=1.3$ kcal., and $\mu_{tg}=2.02$D (calculated moment of $\mu_{tg}=2.37$D).



t,t-form *t,g*-form *g,g*-form

Fig. 3. The three forms considered for dichloromethyl ether

Thus in view of the order of approximation the agreement between the calculated and the observed values are fairly good, which lead to the conclusion that the energy relation discussed above is essentially correct. It is noted that in this case, too, *t,t*-, *t,g*- and *g, g*-forms need not be definite isomers, but represent mean values about their positions

III) Monobromomethyl Ether.—There is a small difference in the moment value in the gaseous state (average moment 2.04D) and in solution (2.18D), but no temperature dependence of the moment in either case[17]. The same discussion as in I) leads to the energy difference between the *trans* form and the *gauche* one or zero or ±∞[18]. The moment value of this compound must be nearly the same or at least slightly less than that of the corresponding form of monochloroether. From the assumption of $\Delta E=0$, the calculated average moment is 2.2D, but from the assumption of $\Delta E=\pm\infty$ the calculated moment is 2.7 or 1.5D using the moment of monochloroether. Therefore, ΔE is considered to be equal to zero.

The comparison of this result with the case of monochloroether is interesting. In I) it is seen that the difference in the electrostatic energy between the *trans* and the *gauche* form is partly reduced by the steric energy difference of Cl and CH_3, but in this case ΔE from the steric energy of Br and CH_3 is so great that the electrostatic one is completely

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[16] The *g,g*-form denotes the configuration in which each CCl bond rotates 120° in opposite direction from the *t,t*-form. The one in which both groups rotate in the same direction is excluded because of the shortness of the Cl, Cl distance: ca. 2.3Å.

[17] We have found that in halogenoethane derivatives when the temperature dependence of the moment is measured both in heptane solution and in gaseous state, ΔE derived from both methods are usually in good agreement, although the moment value itself may differ to some extent. (cf. I. Miyagawa, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 1166 (1954)).

[18] The possibility of free rotation is completely ruled out because of the short distance between Br and CH_3 at *cis* position as mentioned in (I).

cancelled leaving ΔE zero. Since ΔE, originated from electrostatic force, does not differ seriously in these two compounds, the steric one is several hundred calories higher in Br......CH_3 than in Cl......CH_3. This difference in steric energy is estimated to be 1.3 kcal. according to the Lenard-Jones type intermolecular potential used by Miyagawa for the case of halogenoethane derivatives[19]. As this figure depends greatly upon the molecular parameter, especially upon the valence angle, the agreement between the observed and the calculated figure seems fairly good.

IV) ***sym*-Dibromomethyl Ether.**—Temperature range of the measurement is narrow because the solution method has to be used. But the tendency of the temperature dependence of the moment is the same as in dichloroether. The same argument as that used in the dichloroether being applied, it is found from the observed value that the energy difference between the *t, g*- and *g, g*-forms is 0.9 kcal./mol. and $\mu_{tg}=1.9D$. Putting the dipole energy of dibromoether equal to that of dichloroether, then it is easily seen from the same discussion as in (II), that the difference in ΔE between dibromo- and dichloro-ether, is the same as that between monobromo- and monochloro-ether, i.e., 0.7 kcal. This value is compared to the observed one, that is, 1.3—0.9=0.4 kcal./mol.. In taking account of the errors in the experiment and the approximate nature of the treatment it can be said that the agreement is rather good.

Concluding the above discussion, the assumption that the dipole-dipole interaction and the steric repulsion are the main factors of the hindering potential of this kind of molecules holds approximately in the mono- and di-halogenomethyl ethers.

Summary

The temperature dependence of the dipole moment was investigated on monochloromethyl ether (I), *sym*-dichloromethyl ether (II) and monobromomethyl ether (III) in the gaseous state, and (III) and *sym*-dibromomethyl ether (IV) in heptane solution. The moment of (I), (II) and (IV) increases with temperature, while that of (III) does not.

From the observed data the energy difference between the *gauche* and the *trans* position is 0.7 kcal./mol. in (I), and zero in (III). Similarly ΔE's between *t,g*- and *g,g*-form of (II) and (IV) are estimated to be 1.3 kcal. and obtained to be 0.9 kcal./mol. respeetively from the observed results.

These energy values are explained satisfactorily by the electrostatic energy of dipole interaction and the steric energy between non-adjacent groups, which are of reasonable order of magnitudes as compared to the case of haloethane derivatives. The author wishes to express his sincere thanks to Prof. Y. Morino for his kind guidance through this study and to Dr. I. Miyagawa for much valuable advice. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author's thanks are also due.

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[19] I. Miyagawa, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 1177 (1954).