Dipole Moments and Internal Rotation of Some Halogenated Hydrocarbons in the Vapor State

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In the previous papers[1,2] one of the present authors (I. M.) discussed the energy differences in the rotational isomers of some halogenated hydrocarbons. By use of the experimental data two relations were pointed out[1e]. The first one is that the energy difference in these molecules depends mainly upon the configuration of the halogen atoms: that is, 1,2-dichloro-compounds have the energy difference of about 1 kcal./mole, and 1,1,2-trichloro-compounds have very large ones (ca. 2 kcal./mole), while 1,1,2,2-tetrachloro-compounds have vanishingly small ones (<0.4 kcal./mole). (See Table II). This striking result was explained qualitatively by some empirical interatomic potentials[2c].

The second interesting relation was found in the change of energy difference in 1,2-dichloro-compounds by successive substitution of the hydrogen atoms by methyl groups. By assuming that the intramolecular potential is the sum of contributions of the potentials between non-bonded atoms or groups, the observed ΔE's of dichloro-compounds are successfully reproduced. In tri- and tetrachloro-compounds, however, ΔE cannot be re produced so well as in the case of dichloro-compounds, and the qualitative explanation of these ΔE's are made in terms of the change in valence angles and of appropriate interatomic potentials. On the other hand it was inferred by Szasz[3] in his recent paper that the energy difference in *n*-propyl chlorides is very small. The second relation described above, gives 0.3 kcal./mole as the energy difference in this molecule. It is clear, therefore, that the second relation cannot be applied without any modification to such a molecule as *n*-propyl chloride. It is one of the purposes of this report to propose a possible explanation for this situation.

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[1] I. Miyagawa, (a) *J. Chem. Soc. Japan*, **75**, 970 (1954); (b) ibid., 1057; (c) ibid., 1061; (d) ibid., 1162; (e) ibid., 1165.

[2] I. Miyagawa, (a) *J. Chem. Soc. Japan*, **75**, 1169 (1954); (b) ibid., 1173 (c) ibid., 1177.

[3] G. I. Szasz, *J. Chem. Phys.*, **23**, 2449 (1955).

TABLE I

OBSERVED POLARIZATIONS, DIPOLE MOMENTS AND ΔE OF SOME HALOGENATED HYDROCARBONS*

1, 2-Dichloro-2-methylpropane

$MR_D=30.5$ cc. $P_E+P_A=32.0$ cc.

Temp. °K	No. of obs.	Press. range mmHg	Molar polarizn. cc.	Mean deviatn. of polarizn. cc.	Dipole moment *D*.
339	6	68- 82	74.0	0.40	1.52_9
353	6	61- 84	73.0	0.35	1.54_1
384	7	82-144	72.2	0.45	1.63_1
411	6	78-138	71.1	0.41	1.62_4
467	8	106-205	66.6	0.80	1.62_8

$(\mu_g)_{obs.}=2.5$ (assuming $\mu_t=0.49$) $\Delta E=0.9$ kcal.
$(\mu_g)_{calcd.}=3.01$

1, 1, 2, 2-Tetrachloropropane

$MR_D=35.6$ cc. $P_E+P_A=37.4$ cc.

371.6	7	51- 77	75.7	0.50	1.52_8
412.7	6	71- 97	72.4	0.49	1.54_0
467	7	82-111	68.5	0.43	1.54_4

$(\mu_g)_{obs.}=2.0$ (assuming $\mu_t=0.84$) $\Delta E=0.3-0.4$ kcal.
$(\mu_g)_{calcd.}=2.24$

1, 2, 2-Trichloropropane

$MR_D=30.8$ cc. $P_E+P_A=32.3$ cc.

353.5	8	61-101	76.4	0.52	1.59_9
383.2	8	74- 99	73.0	0.37	1.60_0
411.5	6	61-110	71.2	0.12	1.62_1
467.5	7	80-131	67.0	0.19	1.61_9

$(\mu_g)_{obs.}=2.8$ (assuming $\mu_t=1.55$) $E\geqq 2.0$ kcal.
$(\mu_g)_{calcd.}=2.97$

1, 1, 2-Trichloro-2-methylpropane

$MR_D=35.5$ cc. $P_E+P_A=37.3$ cc.

382.5	6	72- 88	90.6	0.41	1.82_9
413.2	8	76-103	87.5	0.52	1.84_5
429.6	7	69-102	84.3	0.43	1.82_0
467.4	7	78-110	80.7	0.59	1.82_5

$(\mu_{asym.})_{obs.}=1.83$ $\Delta E\geqq 1.5$ kcal. ($P_A\leqq 2$ cc.)
$(\mu_{asym.})_{calcd.}=1.76$
$(\mu_{sym.})_{calcd.}=3.09$

1, 2-Dibromopropane

$MR_D=30.6$ cc. $P_E+P_A=32.1$ cc.

353.6	5	61- 82	54.2	0.12	1.13_2
371.1	6	65- 95	54.4_5	0.28	1.16_7
412.4	9	79-108	55.0	0.35	1.24_5
467.2	6	68-109	56.4	0.27	1.36_5

$(\mu_g)_{obs.}=2.48$ (assuming $\mu_t=0$) $\Delta E=1.25$ kcal.
$(\mu_g)_{calcd.}=2.41$

1, 2-Dibromo-2-methylpropane

$MR_D=35.2$ cc. $P_E+P_A=37.0$ cc.

353.6	6	47- 67	60.0	0.42	1.16_5
370.4	13	65- 98	61.0-61.8		1.21-1.23**
411.5	8	70- 91	60.2-62.6		1.25-1.31**

* $P_E+P_A=1.05\,MR_D$ is assumed throughout.

** Slight decomposition of the sample is noticed in these runs.

Experimental

All substances used were prepared by the methods described in Beilstein's Handbooks except those with special indication.

1,2-Dichloro-2-methylpropane and 1,1,2-trichloro-2-methylpropane.—Isobutyl alcohol saturated with hydrogen chloride on cooling, was heated to 120°C in a sealed tube for several hours. Isobutyl chloride thus obtained was chlorinated with chlorine gas in the presence of aluminum chloride. The product was fractionated into 1,2-dichloro-2-methylpropane (b. p. 107.0–108.0°C) and 1,1,2-trichloro-2-methylpropane (162.0–163.0°C).

1,2,2-Trichloropropane and 1,1,2,2-tetrachloropropane.—Monochloroacetone and dichloroacetone were prepared by the method described by S. Mizushima et al[4]. Monochloroacetone was added slowly to phosphorus pentachloride in a flask and the mixture was boiled for an hour. Then 1,2,2-trichloropropane was distilled: b. p. 121–123°C.

1,1,2,2-Tetrachloropropane was obtained by boiling a mixture of dichloroacetone and phosphorous pentachloride for fourteen hours: b. p. 153–154°C·

1,2-Dibromo-2-methylpropane.—A mixture of isobutyl alcohol, sulfuric acid in the weight ratio of 5 : 1, containing sea sand as a catalyser, was boiled and isobutylene thus produced was introduced into a vessel containing bromine: b. p. 148–149°/60 mmHg.

1,2-Dibromopropane.—A mixture of propyl alcohol, concentrated sulfuric acid, and sea sand was boiled. Propylene gas thus produced was introduced into a vessel containing bromine: b. p. 141–142°C.

The apparatus and the procedure for measuring the dielectric constant in the vapor state are described elsewhere[5].

Results

The results of the measurement of dipole moments in the gaseous state are given in Table I. In case when there exist two rigid rotational isomers, the *trans* and the *gauche* forms, the average moment μ at temperature T is given by

$$\mu^2=\frac{\mu_g{}^2 s e^{-\Delta E/RT}}{1+se^{-\Delta E/RT}} \tag{1}$$

where μ_g denotes the moment of the *gauche* form and s the weight factor ratio of the *gauche* form to the *trans* one. When $\log \mu^2$ is plotted against $\log (1/T)$, the curve is parallel to that of $\log (se^{-x}/1+se^{-x})$ vs. $\log x$, since,

$$\log \mu^2=\log \mu_g{}^2+\log(se^{-x}/1+se^{-x}),$$

and

$$\log (1/T)=-\log(\Delta E/R)+\log x.$$

Hence the coordinate of the abscissa and that of the ordinate shifted in order to fit the experimental curve $\log \mu^2$ vs. $\log (1/T)$ to the curve $\log (se^{-x}/1+se^{-x})$ vs. $\log x$, must be equal to $\log \Delta E/R$ and $\log \mu_g{}^2$ respectively*·

Eq. (1) was derived from the assumption of the coexistence of the two separate isomers. Actually molecules are distributed among the whole range of internal rotational angle, depending on the shape of the potential curve, so that it may be more rigorous to take into account all positions of rotation. However, the above treatment assuming Eq. (1) is proved to be valid usually within the error in ΔE of 0.15 kcal./mole[1b].

In Table I are also given the values of ΔE and μ_g obtained from the experimental data by the above treatment. The values of μ_g are compared

TABLE II

ENERGY DIFFERENCE IN ROTATIONAL ISOMERS IN HALOGENATED HYDROCARBONS

Compound	Energy difference (kcal./mole)	
	Observed	Calculated
$H_2ClC\text{-}CClH_2$	$1.10^{a)}$	1.2
$H_2ClC\text{-}CClHCH_3$*	$1.0^{b)}$	
g_1		0.9
g_2		1.2
$H_2ClC\text{-}CCl(CH_3)_2$	$0.90^{c)}$	0.9
$(CH_3)_2ClC\text{-}CCl(CH_3)_2$	$1.30^{d)}$	1.3
$HCl_2C\text{-}CClH_2$	$\geq 2.4^{e)}$, $2.9^{f)}$	
$CH_3Cl_2C\text{-}CClH_3)_2$	$\geq 2.0^{c)}$	
$HCl_2C\text{-}CCl(CH_3)_2$	$\geq 1.5^{c)}$	
$HCl_2C\text{-}CCl_2H$	$0^{e)}$	
$CH_3Cl_2C\text{-}CCl_2H$	$0.4^{c)}$	
$H_2BrC\text{-}CBrH_2$	$1.54^{a)}$	1.5
$H_2BrC\text{-}CBrHCH_3$*	$1.25^{c)}$	
g_1		1.2
g_2		1.5
$H_2BrC\text{-}CBr(CH_3)_2$	$1.1^{g)}$	1.2
$(CH_3)_2BrC\text{-}CBr(CH_3)_2$	$1.6^{d)}$	1.6
$HBr_2C\text{-}CBrH_2$	$\geq 1.5^{g)}$	
$HBr_2C\text{-}CBr_2H$	0, or $-\infty^{g)}$	
$H_2ClC\text{-}CCH_3H_2$	$0^{h)}$	0.3
$H_2BrC\text{-}CCH_3H_2$	$0^{h)}$	0.3

* This molecule has two *gauche* forms, g_1 and g_2.

a) K. Kuratani, T. Miyazawa and S. Mizushima, *J. Chem. Phys.*, **21**, 1411 (1953).

b) Y. Morino, I. Miyagawa and T. Haga, *ibid.*, **19**, 791 (1951).

c) Present results.

d) Y. Morino, I. Miyagawa, T. Haga and S. Mizushima, This Bulletin, **28**, 165 (1955).

e) J. R. Thomas and W. D. Gwinn, *J. Am. Chem. Soc.*, **71**, 2785 (1949).

f) K. Kuratani and S. Mizushima, *J. Chem. Phys.*, **22**, 1403 (1954).

g) I. Miyagawa, *J. Chem. Soc. Japan*, **75**, 1162 (1954).

h) Ref. (10).

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[4] S. Mizushima et al., *J. Chem. Phys.*, **21**, 815 (1953).

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

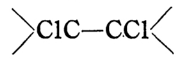
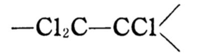
* In case when the moment of trans (μ_t) has a non-zero value, the same relation can hold by taking $\mu^2\text{-}\mu_t{}^2$, and $\mu_g{}^2\text{-}\mu_t{}^2$ in place of μ^2 and $\mu_g{}^2$. Therefore, assuming a finite μ_t, the same procedure can be applied. μ_t is always small and it produces no serious error.

with those calculated by taking empirical induction moments[1c)] into account. It is seen that the agreement between them is fairly good. A little discrepancy in a few cases may be due to the ambiguity of the s-values used. In fact, the change of the s-values exerts sensitive influence on μ_g but not on ΔE.

Discussion

In Table II are summarized the ΔE's obtained both by the present work and by the measurements[1d)] made in solution for the compounds on which the measurement in the gaseous state is difficult owing to the small vapor pressure or thermal decomposition. It is proved that there is practically no difference between the energy difference found in the gaseous state and that in the heptane solution[1e)], so that the energy difference obtained in heptane solution can be compared with those in the gaseous state without any precaution. Table II includes also the results of the related halogenated hydrocarbons which were measured by other authors.

From Table II it is easily seen that ΔE's are grouped into three classes depending on the configuration of chlorine atoms, just as Miyagawa pointed out[1e)].

	configuration	ΔE
1	 $>ClC-CCl<$	ca. 1 kcal./mole
2	 $-Cl_2C-CCl<$	ca. 2 kcal./mole
3	$-Cl_2C-CCl_2-$	ca. 0 kcal./mole

In dichloro-compounds small differences are found from one compound to another depending on the various types of methyl substitution. If the intramolecular potential is given by the sum of these potentials between non-bonded atoms or groups and, further, if it is assumed that the following relations hold between these potentials, the energy differences of many dichloro- and dibromo-compounds calculated are in excellent agreement with the observed:

$$(Cl\cdot Cl)-2(H\cdot Cl)+(H\cdot H)=1.2\,\text{kcal./mole} \tag{2}$$

$$(Cl\cdot CH_3)-(H\cdot Cl)-(H\cdot CH_3)+(H\cdot H)=0.3\,\text{kcal./mole} \tag{3}$$

$$(CH_3\cdot CH_3)-2(H\cdot CH_3)+(H\cdot H)=0.7\,\text{kcal./mole} \tag{4}$$

$$(Br\cdot Br)-2(H\cdot Br)+(H\cdot H)=1.5\,\text{kcal./mole} \tag{5}$$

$$(Br\cdot CH_3)-(H\cdot Br)-(H\cdot CH_3)+(H\cdot H)=0.3\,\text{kcal./mole} \tag{6}$$

where $(A\cdot B)$ denotes a potential difference due to the change of the relative position of the atom pair A and B from the *trans* to the *gauche*.

When the above relation is applied to the case of trichloro and tetrachloro-compounds, the discrepancy between the observed and the calculated becomes apparent. In fact, if the above relation holds, the energy differences of tri- and tetrachloroethane should be just as large as that of dichloroethane. A possible explanation of this discrepancy was presented qualitatively by Mizushima et al. for tetrachloroethane[6)]. The two chlorine atoms attached to the same carbon atom have the $\angle ClCCl$ angle larger than the tetrahedral value and non-adjacent $Cl\cdots Cl$ atoms come closer in the *trans* form. It is expected, therefore, that the *trans* form becomes much less than that in the case when the tetrahedral angle is maintained. If it is assumed that the angle of $\angle ClCCl$ is reduced to the tetrahedral one by the substitution of a methyl group in place of a hydrogen atom of $CHCl_2$— group then the energy difference will be expected to be between those of dichloro- and tetrachloro-ethane. This is what is found in the experiment. The observed valence angles, 111° for $\angle ClCCl$ in methylene chloride[7)], 111.5° for $\angle CCC$ in propane[8)], and 109.5° for $\angle ClCCl$ and 109.2° for $\angle CCCl$ in 2,2-dichloropropane[9)] from the electron diffraction investigation, seem to support the above hypothesis.

Eqs. (3), (6), and (4) correspond respectively to the ΔE's of chloropropane, bromopropane, and n-butane. The energy difference in chloropropane obtained by spectroscopy[10)] is nearly equal to zero, which was confirmed recently by electron diffraction investigation[11)]. Therefore, the energy relation assumed by these equations cannot be applied accurately to n-propyl halide molecules. Recently Szasz[3)] proposed an interesting assumption that between a halogen atom and a methyl group there must be some attractive force, large enough to cancel the so-called steric repulsion. This assumption can explain the

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6) S. Mizushima, Y. Morino and K. Kozima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29**, 111 (1936).

7) L. E. Sutton and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).

8) L. Pauling and L. O. Brockway, ibid., **59**, 1223 (1937).

9) J. W. Coutts and R. L. Livingston, ibid., **75**, 1542 (1953).

10) C. Komaki et al., This Bulletin, **28**, 330 (1955).

11) Y. Morino and K. Kuchitsu, to be published in *J. Chem. Phys.*

extremely small energy difference in *n*-propyl chloride and the related hydrocarbons but it conflicts with the energy relation found in dichloro-isobutane; that is, the observed energy difference in this molecule is considerably lower than that in 1,2-dichloroethane, contrary to what is expected from Szasz's hypothesis. It should be assumed, therefore, that the methyl groups in *n*-propyl halides are quite different from the CH_3 groups in 1,2-dichloro-compounds. It may be probable to assume that the methyl group in *n*-propyl chloride rotates slightly about its symmetry axis to minimize the repulsion between the halogen atom and the methyl group and to make the energy difference small.

According to this assumption the two methyl groups in isobutyl chloride rotate around their axis, keeping some liaison to each other like gears, and this fact also makes the energy difference small. In dichloro-isobutane, on the contrary, the rotation of a methyl group is hindered, probably to a considerable extent, by the chlorine atom attached to the carbon atom. Therefore, the energy difference due to this effect will make the *trans* forms unstable, and, accordingly, decrease the net energy difference from that in 1,2-dichloroethane.

The situation may be the same for the methyl-methyl interaction when a halogen atom is attached to the carbon atom to which one of the methyl groups is attached. The degrees of rigidness of methyl groups in dichloropropane, dichloro-isobutane and 2,3-dichloro-2,3-dimethylbutane may not be perfectly equal to each other. The difference of this effect in the above three molecules, however, is supposed to be small, though it may be one of the origins of a small disagreement between the observed energy difference and the calculated one given in Table II. The energy difference 0.77 kcal./mole of *n*-butane may be a result of the fact that methyl-methyl repulsion cannot be cancelled out perpectly by such a rotation of the methyl group, because van der Waals' distance between the methyl groups, 4.33 Å, is larger than the distance of the methyl groups at the *gauche* position, 3.02 Å.

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[12] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948).