21.93 cal. per mole for $MgTiO_3$. The constants in the equations were calculated by the graphical method described by Shomate,[13] which has the advantage of employing all the measured values rather than a selected few.

$CaTiO_3(\alpha)$: $H_T - H_{298.16} = 30.47T + 0.68 \times 10^{-3}T^2 + 6.690 \times 10^5T^{-1} - 11,389$ (0.6%; 298–1530°K.)

$CaTiO_3(\beta)$: $H_T - H_{298.16} = 32.03T - 11.197$ (0.2% 1530–1800°K.)

$FeTiO_3(s)$: $H_T - H_{298.16} = 27.87T + 2.18 \times 10^{-3}T^2 + 4.793 \times 10^5T^{-1} - 10.111$ (0.3%; 298–1640°K.)

$FeTiO_3(l)$: $H_T - H_{298.16} = 47.60T - 14,642$ (0.1%; 1640–1800°K.)

$MgTiO_3(s)$: $H_T - H_{298.16} = 28.29T + 1.64 \times 10^{-3}T^2 + 6.530 \times 10^5T^{-1} - 10,771$ (0.4%; 298–1800°K.)

The following, corresponding heat-capacity equations were obtained by differentiation.

$CaTiO_3(\alpha)$: $C_p = 30.47 + 1.36 \times 10^{-3}T - 6.690 \times 10^5T^{-2}$

$CaTiO_3(\beta)$: $C_p = 32.03$

$FeTiO_3(s)$: $C_p = 27.87 + 4.36 \times 10^{-3}T - 4.793 \times 10^5T^{-2}$

$FeTiO_3(l)$: $C_p = 47.60$

$MgTiO_3(s)$: $C_p = 28.29 + 3.28 \times 10^{-3}T - 6.530 \times 10^5T^{-2}$

Table IV contains values of the heat contents at even temperatures as read from smooth curves through the experimental data. The entropy increments above 298.16°K. also are included. The latter were obtained from the relationship

$$S_T - S_{298.16} = \frac{H_T - H_{298.16}}{T} + \int_{298.16}^{T} \frac{H_T - H_{298.16}}{T^2}\, dT$$

The last term was evaluated by numerical integration of a plot of $H_T - H_{298.16}/T$ against log T.

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	CaTiO₃		FeTiO₃		MgTiO₃	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
400	2,680	7.73	2,595	7.46	2,500	7.21
500	5,430	13.86	5,330	13.56	5,130	13.07
600	8,300	19.09	8,200	18.78	7,900	18.12
700	11,260	23.65	11,120	23.28	10,790	22.57
800	14,270	27.67	14,150	27.33	13,740	26.51
900	17,310	31.25	17,250	30.97	16,750	30.05
1000	20,380	34.48	20,440	34.34	19,800	33.27
1100	23,490	37.44	23,650	37.38	22,900	36.22
1200	26,640	40.18	26,900	40.22	26,030	38.94
1300	29,820	42.73	30,200	42.87	29,190	41.47
1400	33,030	45.10	33,520	45.32	32,390	43.84
1500	36,270	47.34	36,920	47.67	35,660	46.09
1530	37,260(α)	47.99				
1530	37,810(β)	48.35				
1600	40,050	49.78	40,360	49.89	39,010	48.26
1640			41,750(s)	50.76		
1640			63,420(l)	63.97		
1700	43,250	51.72	66,280	65.68	42,450	50.34
1800	46,460	53.55	71,040	68.41	45,980	52.36

Summary

High-temperature heat contents of the metatitanates of calcium, iron, and magnesium were determined from 298° to temperatures near 1,800°K.

Calcium metatitanate has a transition at 1,530° K., the heat absorption being 550 cal. per mole.

Ferrous metatitanate melts at 1,640°K., the heat of fusion being 21,670 cal. per mole.

Heat-content and heat-capacity equations were derived for each titanate, and a table of smooth, even-temperature heat-content and entropy increment values was included.

BERKELEY, CALIF. RECEIVED FEBRUARY 7, 1946

(13) Shomate, THIS JOURNAL, **66**, 928 (1944).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Resonance in Vinyl Sulfide and Six Unsaturated Chlorohydrocarbons

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

The large lowering of the dipole moment[1] of vinyl chloride and the shortening of the carbon–chlorine bond[2] below the normal single bond length have given evidence of double bond character in the carbon–chlorine bond as the result of resonance involving a structure with positive chlorine linked to the carbon by a double bond. It has seemed of interest, therefore, to investigate the polarities of the three different molecules in which one of the three hydrogens of vinyl chloride is replaced by a methyl group. In addition, three other molecules in which the chlorine is not adjacent to the double bond have been investigated. Analogy between the resonance in vinyl chloride and divinyl sulfide has led to the inclusion of work on the latter substance in this paper.

The dielectric constants of the vapors of these substances were measured with the apparatus and technique previously described and used to calculate the polarizations and dipole moments of the molecules.[3]

Materials

4-Chlorobutadiene-1,2.—Material kindly given us by the du Pont Company was regarded as pure. It was subjected to the usual double distillation required to introduce the vapor into the dielectric cell.

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(1) Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

(2) Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935).

(3) McAlpine and Smyth, *ibid.*, **55**, 453 (1933); deBruyne and Smyth, *ibid.*, **57**, 1203 (1935); Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).

Allyl Chloride, Methallyl Chloride and 2-Chloropropylene.—Pure samples given us by the Shell Development Company through the kindness of Dr. Otto Beeck, were subjected only to the usual double distillation carried out in the vacuum system.

***cis*- and *trans*-1-Chloropropylene.**—Two samples were kindly furnished by the Research Chemicals Company, representing the *cis* and *trans* forms of the compound, although the separation was not known to be better than 90%. The samples boiled in the ranges 32–32.5° and 37–38°, representing the *cis* and *trans* forms, respectively. Kharasch and his co-workers[4] give for the boiling points at 744 mm., for the *cis* form. 32.0–32.2°. and for the *trans*, 36.7°. Timmermans[5] gives for the *cis* form, 32.8°, and for the trans. 37.4°. at 760 mm.

Divinyl Sulfide.—A pure sample was kindly given us by Professor A. von Hippel of the Massachusetts Institute of Technology.

TABLE I

POLARIZATIONS AND DIPOLE MOMENTS

T. °K.	P	$\mu(\times 10^{18})$
4-Chlorobutadiene-1,2		
394.1	88.73	2.03
423.2	84.51	2.03
	85.66	2.04
442.4	83.29	2.05
	81.83	2.03
457.7	78.87	2.01
491.1	75.48	2.01
491.3	74.92	2.00
Allyl Chloride		
377.1	83.70	1.98
	83.58	1.98
	84.20	1.99
396.5	80.56	1.98
	78.70	1.95
	78.77	1.95
419.1	77.94	1.99
	79.20	2.01
	78.10	1.99
	79.13	2.01
443.4	73.22	1.96
	73.92	1.98
	73.14	1.96
	73.48	1.97
480.0	70.09	1.98
	68.86	1.96
	69.00	1.96
	70.27	1.98
Methallyl chloride		
376.8	82.56	1.89
396.3	77.82	1.85
	75.28	1.81
438.8	72.92	1.86
	73.16	1.86
460.7	71.11	1.87
	71.43	1.87
476.8	67.72	1.83
	66.38	1.80
cis-1-Chloropropylene-1		
344.5	72.18	1.71
	72.18	1.71
360.6	69.69	1.71
375.0	68.55	1.72
	67.58	1.71
427.0	61.87	1.71
	61.87	1.71
475.5	58.01	1.71
	56.61	1.68
2-Chloropropylene-1		
338.8	72.62	1.70
	70.38	1.67
	71.79	1.69
383.9	64.75	1.67
	64.51	1.67
	66.90	1.71
	66.83	1.71
410.8	61.89	1.67
	62.59	1.69
	61.81	1.67
	63.36	1.70
431.2	60.56	1.69
	60.80	1.69
	61.70	1.71
445.2	59.92	1.70
	57.93	1.66
	59.92	1.70
468.8	58.30	1.71
	57.86	1.70
	58.04	1.70
trans-1-Chloropropylene-1		
344.5	90.99	2.00
	89.69	1.98
360.5	86.32	1.98
	84.95	1.96
375.0	84.23	1.98
427.0	74.91	1.96
	75.22	1.96
475.5	69.82	1.97
	69.82	1.97
Divinyl sulfide		
400.1	49.19	1.19
420.5	49.93	1.24
428.7	49.45	1.24
	47.26	1.18
433.8	48.47	1.22
	46.93	1.18
461.1	45.86	1.18

Experimental Results

The measurements on allyl chloride and 2-chloropropylene-1 were made by the "two-point" method, in which the dielectric constant was measured at only two pressures, and the other substances were measured by the "extrapolation" method, in which the effects of deviation from the gas laws were eliminated by several measurements over a wide range of pressure. The results of individual runs at each absolute temperature, T, are given in Table I for the molar polarization, P, of all the substances. The dipole moment, μ, was calculated from the equation $\mu = 1.28 \times 10^{-20} [(P - MR_D)T]^{1/2}$, in which the molar refraction, MR_D, was obtained for 4-chlorobutadiene-1,2 from the measurement of Carothers, Berchet and Collins[6] and, for the other substances, was taken or calculated from tables in Landolt–Börnstein (5th ed.).

TABLE II

MOLAR REFRACTION AND DIPOLE MOMENT VALUES

	MR_D	$\mu(\times 10^{18})$
4-Chlorobutadiene-1,2	25.31	2.02
Allyl chloride	20.44	1.98
Methallyl chloride	25.06	1.85
2-Chloropropylene	20.44	1.69
cis-1-Chloropropylene	20.44	1.71
trans-1-Chloropropylene	20.44	1.97
Divinyl sulfide	27.6	1.20

Discussion of Results

The moment of 4-chlorobutadiene-1,2, $CH_2{=}C{=}CH{-}CH_2Cl$, is only 0.07 lower than the value, 2.09, for the corresponding saturated compound, *n*-butyl chloride.[7] The molecule should receive small contributions from structures such as $:\!C^-H_2{-}C^+{=}CH{-}CH_2Cl$ and $CH_2{=}C^+{-}\ddot{C}^-H{-}CH_2Cl$, which, in hydrogen halide addition reactions, would account for the observed addition of the halogen to the carbon marked as positive in these structures and of the hydrogen to one of the adjacent carbons. The lowering of the moment below that of *n*-butyl chloride would be explained by the predominance of the first structure, the moment of which would tend to oppose the principal molecular moment due to the carbon–halogen bond. Actually, the chemical evidence is too conflicting and uncertain to be of much value and the small difference between the moments of the saturated and the unsaturated compounds could also be due to contribution from a structure such as $CH_2{=}\overset{-}{\ddot{C}}{-}CH{=}\overset{H^+}{C}HCl$, which

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[4] Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 301 (1937).

[5] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

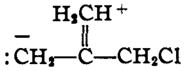
[6] Carothers, Berchet and Collins, THIS JOURNAL, **54**, 4066 (1932).

[7] Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

should have a moment like that of the polar structure $:\overset{-}{C}H_2-\overset{H^+}{C}H=CH_2$, responsible for the moment of propylene.

Although the moment of allyl chloride had already been measured by other investigators, the determination was repeated here in order to obtain a value more certainly comparable with the other results reported in the present paper. The value 1.98 in Table II is in satisfactory agreement with the results of other measurements, 1.97,[8] 1.99,[9] 2.01,[10] and 2.02.[11] The moment, 1.98, is 0.12 lower than the moment found[12] for the corresponding saturated compound, propyl chloride, which is indistinguishable from that of *n*-butyl chloride. This lowering indicates contributions from two forms with propylene-like polarity, such as $:\overset{-}{C}H_2-\overset{H^+}{C}H=CHCl$. Further evidence of this is given by the fact that the addition of hydrogen chloride to allyl chloride gives 1,2-dichloropropane.

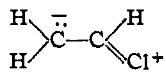
The moment of methallyl chloride, 1.85, is 0.24 lower than that of *n*-butyl chloride and 0.19 lower than that of *i*-butyl chloride,[7] which it should most nearly resemble in the inductive effect of the carbon–chlorine bond moment upon the rest of the molecule. As the lowering of moment, 0.05, from *n*-butyl to *i*-butyl chloride and from *n*-butyl to *i*-butyl alcohol was attributed[7] to such an inductive effect, 0.05 may be taken approximately as the inductive lowering and 0.19 as the lowering due to contributions from polar structures like that written for allyl chloride and from three more important structures, such as



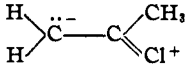
$$:\overset{-}{C}H_2-\overset{\overset{H_2CH^+}{\|}}{C}-CH_2Cl$$

A random orientation of the C–Cl dipole over all possible positions of rotation around the C–C bond would give a resultant moment hardly affected by the polar propylene-like moment of the above structure, while, if the chlorine and the methyl were in a *cis* position about the C–C bond, the moment of the above structure would oppose the carbon–chlorine moment and reduce the molecular moment by, perhaps, as much as 0.35, the moment of propylene. As the lowering of 0.19, apparently due to polar structures, is only 0.05 greater than that found for allyl chloride, it appears that the tendency toward orientation in the *cis* position is small but appreciable. It should be noted further that it is in the region of the *cis* position that the inductive effect lowers the moment.

The lowering, 0.61, of the moment of vinyl chloride, 1.44, below that of ethyl chloride, 2.05, and the shortening of the C—Cl bond 0.07 Å. below the normal single bond value, have been attributed[1,2] to the contribution of the polar structure

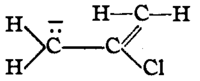


In the case of 2-chloropropylene, a similar contribution from an analogous structure



I

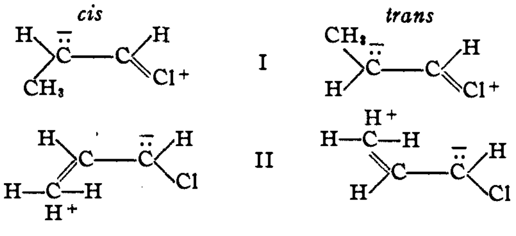
should lower the moment below that of the corresponding saturated molecule of isopropyl chloride, 2.15, to give a value 2.15–0.61 = 1.54. However, as in methallyl chloride, three structures, such as



II

can contribute. The molecular model shows that the moment due to these structures acts at an angle of about 90° to the carbon–chlorine dipole. If its contribution is the same as in the case of propylene, 0.35, the moment is raised by it only from the calculated value, 1.54, to 1.58, as compared to the observed value 1.69. As structure II puts negative charge on the same carbon as does structure I, it may reduce its contribution somewhat below that of the analogous structure for vinyl chloride and, therefore, raise the moment above that of vinyl chloride. The moment 1.69 of 2-chloropropylene would, therefore, be closely accounted for.

Although the samples of the two isomers of 1-chloropropylene were each thought to contain a small amount of the other isomer, the amount contained could not have raised the value observed for the moment of the *cis* isomer by more than 0.03 or lowered that for the *trans* by more than 0.03. For these molecules, contributing polar structures may be written analogous to those for 2-chloropropylene



If the contribution from structure II diminishes that from I, the lowering of the moment by I should be less than in vinyl chloride. That a diminution occurs in isocrotyl chloride is shown by the fact that electron diffraction measurements[13] indicate a shortening of the carbon–chlorine bond less than that in vinyl chloride. In *cis*-1-chloropropylene, the moment contribution of structure II, assumed, as usual, to be the same

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(8) Höjendahl. "Studies of Dipole Moments," Copenhagen, 1928.

(9) Gupta, *Nature*, **125**, 600 (1930).

(10) Mahanti, *Physik. Z.*, **31**, 548 (1930).

(11) Mahanti, *Phil. Mag.*, **20**, 274 (1935).

(12) Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

(13) Beach and Stevenson, THIS JOURNAL, **61**, 2643 (1939).

as that of propylene, 0.35, makes an angle of about 99° with the carbon–chlorine dipole and, therefore, raises the moment by about 0.09. As might be expected, the observed moment, 1.71, is close to that of 2-chloropropylene. In *trans*-1-chloropropylene, the moment of structure II acts so nearly in the direction of the carbon–chlorine dipole that it should raise the resultant moment by about 0.35, that is, 0.26 more than the increase produced by the contribution of the analogous structure for the *cis* compound. This difference, 0.26, is exactly that observed between the *cis* and *trans* moments in Table II. The moment of isocrotyl chloride, $(CH_3)_2C{=}CHCl$, should show an increase over that of *trans*-1-chloropropylene by an amount slightly less than 0.09 as the result of the added *cis* methyl group. In view of the various factors involved, the observed value,[14] 1.99, is in satisfactory agreement with this prediction. The rigidity of these substituted chloroethylene molecules gives a definite geometrical structure and, therefore, more definitely fixed charge distribution than any that can be certainly ascribed to molecules with possibly flexible chains, involving rotation around bonds. The smallness of the discrepancies between the observed and the calculated values may, therefore, be regarded as particularly strong evidence of the correctness of the underlying ideas of charge distribution.

The moment of divinyl sulfide, 1.20, is 21% below the value[15] for diethyl sulfide, 1.51, while the previously discussed moment of vinyl chloride is 30% below the value for ethyl chloride. The lowering of the divinyl sulfide moment is attributable to contributions from two structures, such as $CH_2{=}CH{-}\ddot{S}^+{=}CH{-}^-CH_2$, analogous to the structure written for vinyl chloride, $Cl^+{=}CH{-}\ddot{C}^-H_2$. The lowering of the thiophene moment, 0.54, in solution[16] and 0.58 in the gas,[15] below the value, 1.87, for tetrahydrothiophene in solution,[16] which has been discussed previously,[17] is much greater than that of vinyl sulfide because, in thiophene, the number of possible stable structures with positive sulfur is greater and the restriction by the ring of the directions of their moments gives a larger resultant moment opposing the resultant of the two carbon–sulfur moments. Similarly, the lowering of moment from that of tetrahydrofuran,[16,18] 1.71 in benzene solution, and 1.82 in dioxane solution to that of furan, 0.7 in benzene solution,[18] is much greater than that from diethyl ether, 1.18 in the gas[19] and 1.14 in solution[20] to divinyl ether, 1.06 in solution.[18] The lowering of moment by resonance in these oxygen compounds is somewhat less than in the corresponding sulfur compounds, particularly, in the case of divinyl ether and divinyl sulfide.

Summary

The dielectric constants of the vapors of 4-chlorobutadiene-1,2, allyl chloride, methallyl chloride, 2-chloropropylene, *cis*-1-chloropropylene, *trans*-1-chloropropylene, and divinyl sulfide have been measured over a range of temperature and pressure and used to calculate the dipole moments of the molecules.

The double bonds remote from the chlorine in 4-chlorobutadiene-1,2 and allyl chloride cause only small lowerings of the molecular moments, but the added effect of the methyl group in methallyl chloride gives a propylene-like moment in the hydrocarbon chain and increases the lowering of the moment below that of the corresponding saturated molecule.

The three chloropropylene molecules have moments which conform closely to the requirements of their known geometrical configurations, the moments associated with their component parts, and the effects of resonance, thus giving support to the method of treatment in terms of resonance. In these molecules, as in many others, the effects of resonance lend themselves to vector addition along with the group moments which they affect, although there may be mutual influence of resonance effects with consequent alteration in moment.

The dipole moment of divinyl sulfide gives evidence of lowering by resonance like that in vinyl chloride.

PRINCETON, N. J. RECEIVED FEBRUARY 27, 1946

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[14] Hurdis and Smyth, THIS JOURNAL, 65, 89 (1943).

[15] Kubo, *Sci. Papers Inst. Chem. Res.* (Tokyo), 29, 122 (1936).

[16] Robles, *Rec. trav. chim.*, 58, 111 (1939).

[17] Schomaker and Pauling, THIS JOURNAL, 61, 1769 (1939).

[18] Smyth and Walls, *ibid.*, 54, 3230 (1932).

[19] Groves and Sugden, *J. Chem. Soc.*, 211 (1938).

[20] Fuchs and Wolf, "Hand- u. Jahrbuch der chemischen Physik," Akademische Verlagsgesellschaft, Leipzig, 1935, Vol. VI, Appendix.