peroxides to hydrogen peroxide; that some simple relationships may exist is obvious from the above data.

Summary

A modified iodometric method for the determination of organic peroxides is described.

Certain observations have been made on the formation and decomposition of peroxides in n-butyl ether.

When tri-iodide solution is added to excess sodium thiosulfate in glacial acetic acid, the color fades at a measurable rate. The addition of water of course causes the fading to become practically instantaneous.

Crude rate measurements show that benzoyl peroxide and the peroxides in n-butyl ether are about equally reactive toward iodide in glacial acetic acid, and not much less reactive than hydrogen peroxide in the same medium. The addition of water retards all three reactions about equally.

The Dipole Moments and Structures of Chlorine Compounds of Germanium, Chromium, Selenium and Tellurium

BY C. P. SMYTH, A. J. GROSSMAN AND S. R. GINSBURG

The dipole moments of monochloro and dichlorogermane, chromyl chloride, diphenylselenium dichloride and tellurium tetrachloride have been measured with the object of studying the structures of the molecules and obtaining information as to the magnitudes of the bond moments in the molecules. The moments were obtained with the apparatus and methods previously described,[1,2] with the exception of that of monochlorogermane, which was measured in the vapor state by Mr. R. H. Wiswall, Jr., the dielectric constants being determined at three temperatures so close together that the moment was calculated by subtracting a calculated molar refraction from the polarization. The experimental measurements on solutions of dichlorogermane in carbon tetrachloride carried out by Dr. George L. Lewis already have been published and discussed elsewhere. The value of the moment is included in Table II for comparison with that of monochlorogermane.

Preparation of Materials

Benzene[1] and carbon tetrachloride[2] were purified as in the work previously described.

Monochloro- and Dichlorogermane.—A kilogram of germanite containing 6% of germanium dioxide was obtained from the Foote Mineral Company and treated according to a procedure described by Professor J. H. Müller of the University of Pennsylvania in a communication to Professor N. H. Furman of Princeton University, to both of whom the authors wish to express their grati-

tude. By this procedure germanium was extracted from its ore as the tetrachloride, which was then hydrolyzed to form the dioxide. After the reduction of the latter in an atmosphere of hydrogen, it was combined with magnesium. The resulting germanide, treated with hydrochloric acid in an atmosphere of hydrogen, gave monogermane, which was purified by fractionation and mixed with an equal volume of hydrogen chloride over aluminum chloride as a catalyst according to the method of Dennis and Judy.[3] The resulting monochlorogermane and dichlorogermane were separated by fractionation at low temperatures, between 2 and 3 cc. of monochlorogermane and 1 cc. of dichlorogermane being obtained in the liquid form. In spite of careful fractionation, the samples could not be regarded as very pure. The stability of the monochlorogermane was sufficient to permit of its measurement in the vapor state over a limited temperature range, while decomposition of the dichlorogermane was rendered negligible by measurement in dilute solution.

Chromyl Chloride.—The compound was prepared by the method given by Henderson and Fernelius[4] and distilled at reduced pressure in an apparatus which had been dried by thorough baking.

Diphenylselenium Dichloride.—Material from the Eastman Kodak Company was recrystallized from dry benzene and dried in a vacuum desiccator.

Tellurium Tetrachloride.—Twenty-eight grams of c. p. tellurium in the form of sticks was placed in a distilling apparatus, which was then evacuated and baked. The gently heated tellurium was treated with a slow stream of dry chlorine, which converted it first into a black amorphous mass of tellurium dichloride and then into the white, crystalline tetrachloride. The latter was distilled into a side-arm where it gave an amber liquid, which solidified to white crystals.

(1) Lewis and Smyth, J. Chem. Phys., 7, 1085 (1939).

(2) Lewis and Smyth, THIS JOURNAL, 61, 3063 (1939).

(3) Dennis and Judy, ibid., 51, 2321 (1929).

(4) Henderson and Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., Inc., New York N. Y., 1935, p. 143.

Experimental Results

The dielectric constants ϵ and densities d of the solutions containing mole fraction c_2 of the polar solute and the polarizations, P_1 of the solvent and P_2 of the polar solute, are given in Table I. Table II gives values of the molar refractions MR_D for the D sodium line, calculated as the sum of atomic refractions obtained from Landolt-Börnstein or calculated from refraction data in the literature. The errors in MR_D are too small to have appreciable effect upon the values of the moments except in the case of chromyl chloride, the moment of which is enclosed in parentheses because of its uncertainty. The succeeding columns of Table II list the polarizations P_∞ obtained by extrapolating the P_2-c_2 curves to infinite dilution, except in the case of mono-chlorogermane, where P_∞ was obtained from measurements of the vapor at several different pressures, and the dipole moments μ. The measurements on diphenylselenium dichloride were made at 50° in order to take advantage of the greater solubility at the higher temperature.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_1	ϵ	d	P_2
Carbon Tetrachloride–Chromyl Chloride ($t = 25°$)			
0.00000	2.236	1.5836	(28.35 = P_1)
.04836	2.258	1.5986	30.36
.09677	2.283	1.6171	30.13
Benzene–Diphenylselenium Dichloride ($t = 50°$)			
0.00000	2.224	0.8484	(26.67 = P_1)
.01110	2.403	.8679	289.0
.01786	2.505	.8782	281.6
Benzene–Tellurium Tetrachloride ($t = 25°$)			
0.00000	2.276	0.8729	(26.68 = P_1)
.00761	2.352	.8903	165.8
.00981	2.372	.8947	164.1
.01189	2.389	.8991	159.7

TABLE II

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ ($t°$)	$\mu \times 10^{18}$
GeH$_3$Cl	16.93	111.0(3.4°)	2.06
		105.0(14°)	2.03
		99.4(24°)	2.00
		Mean value	2.03
GeH$_2$Cl$_2$	21.8	123(25°)	2.21
CrO$_2$Cl$_2$	26	30.6(25°)	(0.47)
(C$_6$H$_5$)$_2$SeCl$_2$	74	301.2(50°)	3.47
TeCl$_4$	35	167(25°)	2.54

Discussion of Results

As germanium tetrachloride has been found by means of electron diffraction[5] to be tetrahedral, it is practically certain that monochloro and dichlorogermane are approximately tetrahedral. This means that, with inductive effects neglected, the resultant of the moments associated with the three hydrogen–germanium bonds in the mono-chlorogermane molecule should be equal to the moment of one bond and should lie in the line of the germanium–chlorine bond moment, that is, (H–Ge) + (Ge–Cl) = μ_{GeH_3Cl}, where the symbols in parentheses represent the bond moments. Also 1.15 (H–Ge) + 1.15 (Ge–Cl) = $\mu_{GeH_2Cl_2}$. If the bond moments depended wholly on intrinsic electronegativities of the two bonded atoms and were uninfluenced by induction, resonance effects and possible unknown factors, the moments of tetrahedral molecules like these germanes should be independent of the central atom and should depend simply on the differences in electronegativity of the attached atoms. This would mean that both methyl chloride and monochlorogermane would have the same moment as hydrogen chloride, 1.05×10^{-18}. The large effect of complicating factors in raising the carbon–chlorine, –bromine, and –iodine bond moments above the values to be expected on the basis of hydrogen bond moments has been pointed out previously.[6] It is evidently even greater in the case of the germanium–chlorine bond moments, as shown by the large moments of these chlorogermanes. In the case of the chloro-silanes[7] and silicobromoform,[2] the complicating factors seem to compensate one another to such an extent that the moments are not far from the values to be expected on the basis of hydrogen bond moments. The value of the moment of monochlorogermane is in accordance with the ideas previously presented[2] in connection with the relation of the moment of dichlorogermane to the moments of carbon, silicon and tin compounds. As the H–C moment is only about 0.3 and as the H–Ge moment is undoubtedly lower than this, possibly, acting in the opposite direction, it may be concluded that the Ge–Cl moment is about 2, or larger than this by the amount of the Ge–H moment.

For comparison of the moments of the two

(5) Brockway, Rev. Modern Phys., 8, 231 (1936).

(6) Smyth, J. Phys. Chem., 41, 209 (1937); THIS JOURNAL, 60, 183 (1938).

(7) Brockway and Coop, Trans. Faraday Soc., 34, 1429 (1938).

chlorogermanes, it is desirable to use the gas value 2.34 calculated empirically[2] for dichlorogermane from the solution value given in Table II. In the absence of mutual induction between the dipoles in the molecule, the tetrahedral angle 110° requires a ratio 1.15 between the moment of GeH_2Cl_2 and that of GeH_3Cl as between the moments of the corresponding compounds of carbon, silicon and tin.[6] The observed ratios are: for CH_2Cl_2 and CH_3Cl, 0.85; for SiH_2Cl_2 and SiH_3Cl, 0.91; for GeH_2Cl_2 and GeH_3Cl, 1.15; and for $(C_2H_5)_2SnCl_2$ and $(C_2H_5)_3SnCl$, 1.12, as compared to 1.02 for $(CH_3)_2CCl_2$ and $(CH_3)_3$-CCl. Increase in size of the central atom of the tetrahedral molecule with consequent increase in the distance between the attached dipoles evidently decreases the mutual inductive effects of these dipoles, as would be expected.

A moment value as small as that found for chromyl chloride is necessarily uncertain when determined in solution because of neglect of atomic polarization as well as possible solvent effect. The uncertainty of the value in Table II is increased by an uncertainty of 2 cc. in the molar refraction. It is certain, however, that the moment is little larger than 0.5 and probable that it is between 0.5 and 0. If the molecule were tetrahedral and the bond moments unaffected by complicating factors, the moment should be 1.15 times the difference between the Cr–O and the Cr–Cl bond moments. The former bonds are more or less semipolar and should, therefore, have moments not far from 3, although they may have a considerable amount of double bond character, which would lower the moments somewhat. The Cr–Cl bond may be written as a normal covalent bond, but it must be remembered that the Sn–Cl bond was found[6] to have a moment not less than 3.1. It is, therefore, not only reasonable to suppose that the Cr–Cl moment may be of this magnitude but necessary to conclude that it is at least almost as large as this in order to account for the small moment of the CrO_2Cl_2 molecule since the Cr–O moment would be large even if it possessed a good deal of double bond character. The distortion of the tetrahedral structure of this molecule indicated tentatively by electron diffraction,[8] according to which the O–Cr–O angle is about 105° and the Cl–Cr–Cl angle about 113°, would increase the moment of the molecule if the Cr–O moment is greater than the Cr–Cl moment.

A large Cr–Cl moment also accounts for the difference between the small CrO_2Cl_2 moment and the considerable value 1.86 found[9] for SO_2Cl_2, which is due to the difference between the fairly large moment of the more or less semipolar S–O bonds and the small moment 0.5 of the normal covalent S–Cl bonds.

The molecules of diphenylselenium dichloride and tellurium tetrachloride present essentially the same structural problem when treated according to the methods used by Pauling.[10] One might expect to find hybridized sp^3 orbitals, which would give a regular tetrahedral structure with the selenium or tellurium atom at its center, or sp^2d orbitals, which would give a square structure around the central selenium or tellurium atom. Either of these two structures could be reconciled with the moment found for diphenylselenium dichloride, but both would obviously give zero moment for tellurium tetrachloride in contrast to the large value observed. If the $TeCl_4$ molecule were tetrahedral in form and had zero dipole moment, the substance should be soluble in carbon tetrachloride and probably in carbon bisulfide and heptane, in all three of which it was found to be too insoluble to permit of dipole moment measurements. Also its boiling point, instead of being 414°, should not be far from the region 60–114°, in which the boiling points of the symmetrical tetrahedral molecules of carbon, silicon, germanium and tin tetrachloride lie. The symmetrical tetrahedral titanium tetrachloride boils at 136.4°. The symmetrical tetrahedral structure for tellurium tetrachloride would thus be ruled out on the score of its boiling point and solubility in the absence of other evidence. The markedly greater solubility of the compound in benzene than in carbon tetrachloride, carbon bisulfide or heptane suggests the possibility of the formation of an intermolecular compound with the solvent, but the solubility, about 0.012 mole fraction of tellurium tetrachloride at 25°, is still so small that it cannot be regarded as evidence of compound formation, the occurrence of which would probably give rise to a considerable moment. Consequently, we feel sufficient confidence in the moment of the tellurium tetrachloride molecule to rule out both the regular tetrahedral and the square structures for it and also for the diphenylselenium dichloride molecule.

(8) Palmer, THIS JOURNAL. 6ⁿ 2360 (1938).

(9) Smith, *Proc. Roy. Soc.* (London), **138**, 154 (1932).

(10) See Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

According to a treatment of directed valence communicated to us by Professor G. E. Kimball of Columbia University, the tellurium tetrachloride molecule should be an unsymmetrical tetrahedron, which would, of course, possess a moment. An analogous unsymmetrical tetrahedral structure would be indicated for diphenylselenium dichloride. Professor Linus Pauling, who has very kindly read this manuscript, suggests, in view of the moments possessed by these two compounds, that "the configuration is similar to that of PCl_5 and related molecules; that is, that the four bonds and one unshared pair occupy the five corners of a trigonal bipyramid. The unshared pair would probably occupy one of the equatorial positions rather than one of the apical positions." Such a structure would give an unsymmetrical tetrahedral arrangement of the four atoms or groups attached to the central atom, somewhat different from that given by Kimball's treatment.

In order to give rise to molecular moments as large as those observed, the Se–Cl and Te–Cl moments would have to be much larger than the values, 0.6 and 0.9, respectively, calculated on the basis of the electronegativities of the elements.[11] Comparison with the As–Cl value 1.64 and the Sb–Cl value 2.6 suggests 1.2 and 2.3 as possible values for Se–Cl and Te–Cl, respectively, the higher values probably arising from induced shifts of charge. The small moment of the C–Se bond, 0.9, calculated from that of diphenyl selenide cannot contribute largely to the moment of diphenylselenium dichloride, but the high value of this latter moment may be due, at least in part, to the occurrence of resonance with contributions from twelve polar structures such as

(11) See ref. 6 and ref. 10, p. 64.
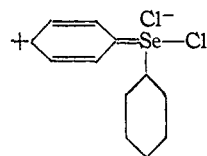
The writers wish to express their indebtedness to Mr. R. H. Wiswall, Jr., for measuring the monochlorogermane and to Dr. J. Y. Beach and Professors G. E. Kimball and Linus Pauling for their advice on the structures of diphenylselenium dichloride and tellurium tetrachloride.

Summary

The dipole moment of monochlorogermane has been measured in the vapor state and the moments of chromyl chloride, diphenylselenium dichloride and tellurium tetrachloride have been measured in solution. The ratio of the moment of monochlorogermane to the previously published value of dichlorogermane shows that the large size of the germanium atom largely eliminates induction between two chlorines attached to it. The considerable value of the moment of the molecule shows that the Ge–Cl bond moment is about 2 or greater than this by the amount of the small Ge–H moment. The very small moment of chromyl chloride shows that the Cr–Cl bond is of the same magnitude as the more or less semipolar Cr–O moment and probably, therefore, as large as 3.

The large moments found for diphenylselenium dichloride and tellurium tetrachloride indicate unsymmetrical tetrahedral structures for their molecules. The Se–Cl and Te–Cl bond moments necessary to produce such moments are much larger than those calculated as the electronegativity differences between the elements.