2. The entropy at 298.1°K. of MoO_3 is found to be 18.68 ± 0.3 cal./°C. and of WO_3 is 19.90 ± 0.2 cal./°C.

3. The complete ΔF^0 equations of formation of the two oxides have been computed.

The Carbides of Magnesium[1]

BY WALTER H. C. RUEGGEBERG

The carbides of magnesium have attracted the attention of investigators for many years.[2]

The work of Novak[3] on these compounds is by far the most illuminating to date. Novak allowed acetylene, methane, n-pentane, n-octane, benzene, toluene and xylenes to react with magnesium metal at elevated temperatures. This work led to the conclusion that there were two carbides of magnesium, namely, the acetylide MgC_2 and a carbide which, upon hydrolysis, gave methylacetylene. To this latter substance, Novak assigned the formula Mg_2C_3, in which, according to this investigator, there should exist discrete C_3^{-4} units in the crystal lattice. Unfortunately, the results of Novak are based upon the hydrolysis products, rather than upon the identification of the crystal modifications.

This paper will constitute a reconsideration of the magnesium carbide problem.

Preparation of the Carbide Mg_2C_3

Four to five grams of powdered magnesium metal was placed in a porcelain boat and the boat and its contents were heated in a stream of gaseous n-pentane at 700°. The hydrocarbon was brought to the metal by bubbling dry hydrogen through n-pentane, thus carrying the vapors through the resistance furnace. It is simply a modification of the general method of the preparation of the alkaline earth carbides, namely

<div align="center">Metal + Carbon ⟶ Carbide</div>
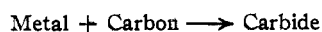
It may be mentioned that magnesium carbide forms in large amounts, if: 1. A hydrocarbon is used which decomposes into large quantities of carbon at the melting point of magnesium (651°). 2. The absence of oxygen is assured. Either gaseous oxygen or an oxide reactant will poison the formation of the carbide by forming the oxide of magnesium. 3. The hydrocarbon does not polymerize into oils or solids to cover the surface of the metal.

X-Ray powder pictures were taken of the carbide resulting from n-pentane and magnesium at 712°. Two separate pictures were made, one of a sample from the surface material in the boat (Table I), the other from the material near the bottom of the boat (Table II). The results clearly indicate complete reaction on the surface, while the lower regions contain large quantities of unchanged magnesium.

TABLE I

Powder Photograph Data of Mg_2C_3 prepared from n-Pentane and Magnesium at 712°
Filtered Cu radiation; sample from top of boat

Relative intensity	d, Å.
Strong	3.21
Very weak	3.05
Very weak	2.74
Strong⁻	2.43
Strong⁻	2.20
Very very weak	2.11
Very very weak	1.97
Medium	1.85
Weak	1.79
Weak	1.75
Weak	1.54
Very weak	1.48

The results here obtained are in full agreement with those previously published for the same substance.[4a,b]

Hydrolyses of the Carbides.—The hydrolyses of the carbides and the identification of the acetylene and methylacetylene were carried out in a manner similar to that described by Novak.[3]

Reaction of Mg_2C_3 with Nitrogen.—Dry oil-pumped nitrogen was passed over magnesium carbide at 620° for two hours. At the end of this time, considerable decomposition of the carbide

(1) From a dissertation submitted by Walter H. C. Rueggeberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University. Original manuscript received November 29, 1941.

(2) For a review of earlier work on this subject, see Gmelin's "Handbook," 8th edition: Magnesium, part B, pp. 299–301 (1939).

(3) Novak, Ber., 42, 4209 (1909); Z. physik. Chem., 73, 513 (1910).

(4) (a) Hanawalt, Rinn and Frevel, J. Ind. Eng. Chem., Anal Ed., 10, 457 (1938). (b) Franck, et al., Z. anorg. Chem., 232, 111 (1937).

TABLE II

Powder Photograph Data of Mg_2C_3 prepared from n-Pentane and Magnesium at 712°

Filtered Cu radiation; sample from bottom of boat

| Relative intensity	Mg (3)	d, Å.	Mg_2C_3, Å.
Medium		3.19	3.21
Very very weak		3.04	3.05
Medium⁻		2.78	2.74
Weak	2.60	2.59	
Strong		2.42	2.43
Weak		2.195	2.20
Weak		2.10	2.11
Weak	1.90	1.89	
Weak		1.845	1.85
Medium		1.60	1.58
Weak⁺		1.535	1.54
Weak⁺	1.47	1.468	
Very weak ?		1.44	
Very weak	1.38	1.375	
Weak		1.358	
Very weak	1.34	1.338	
Very weak	1.22	1.212	
Very weak	1.08	1.098	
Very weak	1.03	1.025	
Very weak	0.974	0.970	

had occurred. The hydrolysis products contained ammonia together with large quantities of elementary carbon. The reaction may be represented by the equation

$$3Mg_2C_3 + 2N_2 \longrightarrow 9C + 2Mg_3N_2$$

or, perhaps more correctly, by

$$3C_3^{-4} + 2N_2 \longrightarrow 9C + 4N^{-3}$$

Reaction of Mg_2C_3 with Carbon Dioxide.—It was observed that carbon dioxide at 600° caused the surface of the carbide to become much lighter in color. This color change was attributed to the formation of magnesium oxide. The carbide, after a two-hour treatment with carbon dioxide, still gave large quantities of methylacetylene upon hydrolysis, but a definite reduction of the carbon dioxide was observed. This indicates that the reaction of the carbide with carbon dioxide is much slower than the reaction of the carbide with nitrogen at the same temperature. The over-all reaction is represented by the equation

$$5CO_2 + Mg_2C_3 \longrightarrow 2MgO + 8CO$$

or

$$5CO_2 + C_3^{-4} \longrightarrow 2O^{-2} + 8CO$$
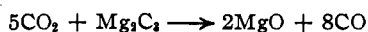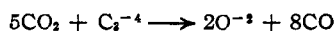
The Acetylide of Magnesium

From Acetylene and Magnesium.—At about 450°, acetylene reacts with magnesium metal to give a substance which upon hydrolysis gives some acetylene. Its formation appears to be confined to the surface of the magnesium metal

granule and may be considered to be a metal–acid reaction represented by the equation

$$Mg + H_2C_2 \longrightarrow MgC_2 + H_2$$
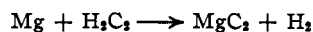
Both the quantity and the quality of MgC_2 formed by this method are by no means satisfactory. Magnesium acetylide is formed, together with elementary carbon and free, unreacted magnesium. An X-ray powder picture of a 450–460° sample was taken. The picture clearly indicated that MgC_2, although perceptible by hydrolysis, is confined to the surface of the magnesium metal granule, the bulk of the material being pure magnesium metal. The results are shown in Table III.

TABLE III

Powder Photograph Data of Mg Treated with C_2H_2 at 460° Using Filtered Cu Radiation

Relative intensity	d	Mg
Medium⁺	2.79	2.77
Medium⁺	2.61	2.60
Very strong	2.45	2.45
Medium	2.11	?
Medium	1.903	1.90
Medium⁻	1.605	1.60
Medium⁻	1.477	1.471
Medium	1.371	1.378
Weak	1.348	1.341
Very weak	0.976	0.974

From Acetylene Di-magnesium Bromide.—Grignard reagents in general are represented by the equilibrium

$$2R-Mg-X \longrightarrow Mg\diagup\diagdown{}^R_R + MgX_2$$
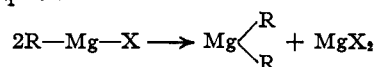
For this reason it seemed advisable to prepare a di-magnesium halide of acetylene.

Ethylmagnesium bromide was prepared in the usual manner, using dry ethyl ether as solvent, in a 3-necked 500-cc. balloon flask; 12 g. of magnesium filings was used in this preparation. After the C_2H_5-MgBr had thus been prepared, dry acetylene gas was bubbled through the solution. After one and a half hours, the solution became viscous and soon solidified to a gel.

Acetylene di-magnesium bromide, Br-Mg-C≡C-Mg-Br, loses its Grignard activity after standing for several weeks. At this time, the substance will still, however, react with water, liberating acetylene. Kleinfelter[5] has explained this phenomenon by assuming that the equilibrium of the acetylene di-magnesium bromide is completely shifted toward the dissociated form. The attainment of this equilibrium is hastened by

(5) Kleinfelter, *Ber.*, **62**, 2736 (1929).

such substances as bromobenzene, chloroform, ethylene dibromide, or by heat

$$Br—Mg—C\equiv C—Mg—Br \longrightarrow MgBr_2 + MgC_2$$
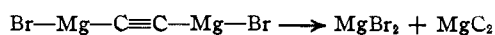
Samples of acetylene di-magnesium bromide (2-3 g.) were placed in a porcelain combustion boat and heated to temperatures ranging from 100–350°. Four X-ray pictures were taken of the resulting material. These, however, showed no clear lines, but only a general blackening of the film. All the heated products reacted with water to liberate acetylene.

At 400°, the acetylene di-magnesium bromide begins to blacken due to the liberation of elementary carbon. A sample of acetylene di-magnesium bromide was heated in an atmosphere of dry hydrogen to 450° for one and a half hours. A highly porous solid remained, which was darkened considerably due to the deposition of free carbon. A lump of the substance, when brought into the tip of a bunsen flame, began to glow, and continued to do so when removed from the flame. Free bromine, carbon, and magnesium oxide were liberated in the process.

The material heated to 450° was extremely reactive toward water, liberating acetylene and hydrogen bromide.
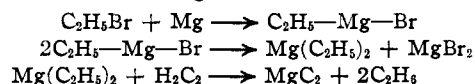
A second sample of acetylene di-magnesium bromide was heated to 600° for one and a half

Fig. 1.—Apparatus for making magnesium acetylide.

hours in a current of dry hydrogen. The hydrolysis of the resulting product yielded methylacetylene

$$2Br—Mg—C\equiv C—Mg—Br \longrightarrow Mg_2C_3 + 2MgBr_2 + C$$
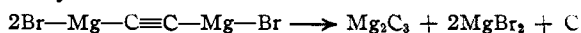
Magnesium Acetylide from Magnesium Diethyl.—The undesirable by-product $MgBr_2$ in the decomposition of acetylene di-magnesium bromide suggested a reaction in which the by-product would be gaseous, namely, the displacement of ethane from magnesium diethyl by acetylene.

Ethylmagnesium bromide was prepared in the usual manner in an apparatus as shown in Fig. 1. Dry 1,4-dioxane was added to the freshly prepared Grignard reagent until no more precipitate came down. After letting the product stand for one to two hours, it was filtered through the dry asbestos mat and allowed to drop into an ether solution of acetylene. A white precipitate resulted almost instantly. After completion of the reaction, the excess solvent was drawn off under suction with slight heating (100°). White magnesium acetylide, MgC_2, remained. At 400° the substance began to darken with the elimination of carbon. The acetylide reacted with water vigorously to liberate acetylene and elemental carbon. In several hydrolyses, especially in the presence of insufficient quantities of water, MgC_2 will hydrolyze to burst into flame. The reactions involved in this method of preparation are the following

$$C_2H_5Br + Mg \longrightarrow C_2H_5—Mg—Br$$
$$2C_2H_5—Mg—Br \longrightarrow Mg(C_2H_5)_2 + MgBr_2$$
$$Mg(C_2H_5)_2 + H_2C_2 \longrightarrow MgC_2 + 2C_2H_6$$

Extreme care must be taken in the preparation of the asbestos mat in the filter, since some bromide is very apt to leak through and contaminate the sample of acetylide. The entire apparatus of course must be thoroughly dry.

Several X-ray powder pictures were taken of MgC_2, both in ether suspension and as a dry solid. It was extremely difficult to obtain a good picture. Table IV gives the data obtained from a sample dried at 100° in vacuum.
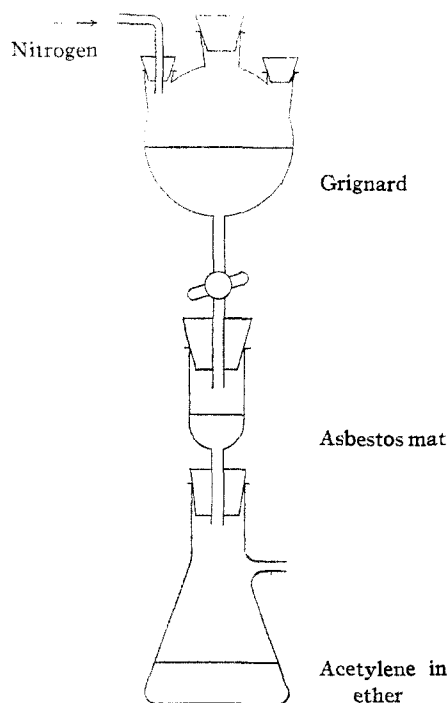
TABLE IV

MgC_2 from $Mg(C_2H_5)_2$, Filtered Mo Radiation

| d, Å.	Intensity[6]
1.27	Very weak
1.51	Weak
1.83	Weak
2.17	Very very weak
2.49	Weak

(6) The relative intensities given here were obtained by comparing them with those of the Mg_2C_3 samples previously determined.

Franck, et al.,[4b] in their work on CaC_2 also prepared samples of Mg_2C_3 and MgC_2. As previously stated, their powder photograph data on Mg_2C_3 agree within experimental errors with those presented in this work.

As for MgC_2, it may be mentioned that due to the scarcity of lines in the powder photograph, complete comparison with Franck's data was impossible. However, the lines appearing on the photograph correspond to the strongest lines obtained by Franck. It appears, also, that the impurities (one of which probably was graphite) in Franck's sample could well be responsible for some of the lines in his analysis.

Consideration of the Formation of Methylacetylene

The alkaline earth carbides are true acetylides with the general formula MC_2. Beryllium occupies a unique position in this family of metals in that it forms the methanide Be_2C. Aside from its non-stability toward heat, MgC_2 offers no particular difficulty in this group. Its transformation to Mg_2C_3, however, creates a problem which requires some consideration. The position of magnesium intermediate between beryllium and calcium may conceivably suggest the dual character of the magnesium carbides. That is to say, there is an MgC_2 analogous to CaC_2, and one could postulate an Mg_2C analogous to Be_2C. According to this reasoning, Mg_2C_3 could be a mixture of MgC_2 and Mg_2C such that

$$3Mg_2C_3 = 4MgC_2 \cdot Mg_2C$$
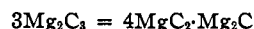
If this formula for Mg_2C_3 were correct, then the hydrolysis of this substance should be represented by the equation

$$C^{-4} + 4(C{\equiv}C)^{-2} + 12H_2O \longrightarrow$$
$$CH_3C{\equiv}CH + 12OH^- + H_2 + 3HC{\equiv}C{-}H$$
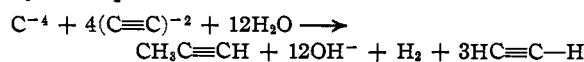
This type of mechanism would fall back on the free radical hydrolysis mechanisms, already suggested by Schmahl[7] and by Schmidt.[8] Examination of this equation immediately raises several points: (1) The hydrogen produced in the reaction would reduce considerable quantities of the methylacetylene to more saturated hydrocarbons. (2) The preponderance of MgC_2 in the hypothetical formula $4MgC_2 \cdot Mg_2C$ should always give rise to the evolution of acetylene in considerable quantities, upon hydrolysis. (3) The presence of the methanide should give some

(7) Schmahl, Z. Elektrochem., 40, 68 (1934).

(8) Schmidt, ibid., 40 170 (1934).

methane upon hydrolysis, or CBr_4 when Mg_2C_3 is treated with bromine. (4) A free radical mechanism should give rise to compounds with more than three carbon atoms per molecule. All the expected properties for such a composition are contrary to experimental fact. In order to prove these points conclusively, some reactions were performed, which, according to the picture of hydrolysis just described, should give rise to compounds that yield methylacetylene upon hydrolysis.

Mechanical Mixture of a Methanide and an Acetylide.—Aluminum carbide, Al_4C_3, and calcium carbide, CaC_2, were ground together to a fine powder. When the resulting mixture was hydrolyzed, the products were acetylene and methane. No trace of methylacetylene could be detected.

Hydrolysis of a Methanide and an Acetylide of a Single Cation.—Both beryllium and aluminum,[9] when treated with acetylene gas at elevated temperatures, regenerate some acetylene upon hydrolysis. If these compounds are heated to still higher temperatures, one should expect that these inferred acetylides of beryllium and aluminum would go over into their stable carbides, Be_2C and Al_4C_3, respectively. During the course of this transformation there should be, at some temperature, a sufficient quantity of both the methanide and the acetylide, so that upon hydrolysis methylacetylene should be generated.

Beryllium metal shavings were heated in a stream of acetylene at temperatures ranging from 400–500°. The deposition of carbon on the metal was considerable, especially around 500°. Upon hydrolysis, however, no methylacetylene could be detected.

Beryllium metal was also heated with n-hexane over a temperature range up to 860°. Hydrolysis of these products yielded no methylacetylene. The 860° product contained small crystals of Be_2C on its surface. At temperatures greater than 860°, the decomposition of hydrocarbons on the metal may prove to be a workable method for the preparation of Be_2C.

Aluminum was allowed to react with acetylene in the same manner as the beryllium described above. No methylacetylene could be found.

n-Hexane was also allowed to react with aluminum turnings at temperatures up to 860°. Although this temperature is well above the melt-

(9) Durand, Bull. soc. chim., 35, 1141 (1924).
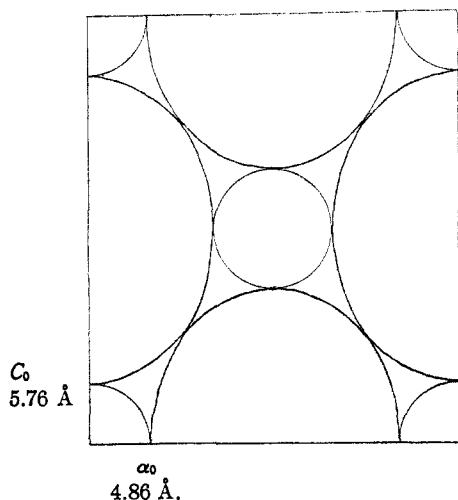
C_0
5.76 Å

a_0
4.86 Å.

Fig. 2.—The 100 plane of magnesium acetylide.

ing point of this metal, the turnings retained their shapes. On their surfaces, however, were large deposits of carbon, and a trace of a substance which appeared to be the methanide Al_4C_3. At temperatures greater than 860°, the solution of carbon in the metal may prove to be more rapid, so that the decomposition of hydrocarbons on the metal may become a method for making Al_4C_3. No methylacetylene could be found in any of the hydrolysis products obtained from these preparations.

Magnesium Carbide and Bromine.—Bromine dissolved in carbon tetrachloride was allowed to stand with Mg_2C_3 for one month. At the end of this period, 0.5 cc. of a heavy liquid was isolated, from which no carbon tetrabromide, CBr_4, could be isolated.

Excess Carbon on an Acetylide.—It has been observed that in the presence of carbon, a carbide may be hydrolyzed to give hydrocarbons of larger molecular weight,[10] that is to say, more carbon atoms per molecule, than are found when the same carbide is hydrolyzed without excess carbon. This phenomenon suggested that perhaps the acetylide CaC_2, when heated to 700° in the presence of n-hexane, would deposit enough carbon to give a substance which upon hydrolysis might give hydrocarbons of greater molecular weight than acetylene. The results of this experiment clearly indicated the presence of acetylene, only.

From these results, it may be stated that the more stable carbide of magnesium, Mg_2C_3, by chemical tests, proves to be a pure substance.

It is not the acetylide with excess carbon, which could be held responsible for the formation of methylacetylene.

The Stability of Magnesium Acetylide.—Stackelberg[11] has determined the structures of the alkali and the alkaline earth carbides, and has shown that these are of a tetragonal structure. Figure 2 represents the distribution of the cations and anions, $(C≡C)^{-2}$, of the 100 plane. The diagram indicates clearly that the structure of the compound is determined by the large acetylide ions. This means that the variations in the constants of the unit cell a_0, b_0 and c_0 are due to the varying sizes of the cations in going from calcium to barium.

It may be seen, by considering a cation bounded by four acetylide ions, that the hole surrounded by acetylide ions assumes a limiting dimension as the size of the cation diminishes. Stated conversely, with diminishing cation radius, anion repulsion increases.

With the aid of the Stackelberg model, some calculations may be made for MgC_2. Assuming the radius of the magnesium ion to be of the order of 0.78 Å. the unit cell of magnesium should have the dimensions

$$a_0/4.86\ \text{Å}. \qquad c_0/5.76 \qquad c_0/a_0/1.185$$

The size of the magnesium ion will thus give a structure which leads to considerable anion repulsion. The structure of MgC_2, therefore, represents the limit of stability for the alkaline earth acetylides. At an elevated temperature, the anion repulsion effect becomes more pronounced and, therefore, MgC_2 will break down to form carbon and its other, more stable, carbide, Mg_2C_3.

Using the lattice constants for magnesium acetylide on the X-ray powder photograph which was obtained from the reaction product of acetylene and magnesium diethyl, one obtains the interesting result given in Table V. The d's were calculated from the equation

$$\frac{4\sin^2\theta}{\lambda^2} = \frac{n^2}{d^2} = \frac{1}{a_0^2}\left[h^2 + k^2 + \frac{l^2}{(c_0/a_0)^2}\right]$$

Analogy with the Peroxides.—An interesting analogy to the acetylides of the alkaline earth metals is offered by the peroxides of these metals. The peroxides contain the O_2^{-2} unit in their crystal lattice, entirely analogous to the C_2^{-2} ion found in the acetylides. The stable peroxides

(10) Lebeau and Damiens, Compt. rend., 156, 1987 (1913).

(11) Stackelberg, Z. physik. Chem., B9, 437 (1930).

TABLE V

h k l	Expected d, Å.	d found, Å.
1 1 Ī	2.94	
0 0 2	2.88	
2 0 0	2.44	2.48
2 0 2	1.85	1.83
2 2 0	1.72	
1 1 3	1.68	
3 1 1	1.49 ⎫	
2 2 2	1.47 ⎭	1.51
2 0 4	1.24 ⎫	
4 0 0	1.22 ⎭	1.27

A faint line with $d = 2.17$ could not be accounted for; however, it was observed that this line occurred also with medium intensity in samples of pure magnesium, and hence was a line foreign to the sample.

of the alkaline earths are CaO_2, SrO_2, and BaO_2. As the radius of the cation decreases, the stability of the corresponding peroxide falls off also. The peroxide of magnesium is usually written as $MgO \cdot MgO_2$ which readily loses oxygen.

It is hoped that more work on the carbides of magnesium will be done by this author in the future.

Acknowledgments

The author desires to express his sincerest thanks to Professor J. C. W. Frazer for his continued interest and guidance in this work. He also wishes to express his gratitude to the Hynson, Westcott and Dunning Fund for financial assistance, which helped to make this work possible.

Results

1. It has been shown that the acetylide MgC_2 is a compound unstable at elevated temperatures, thereby liberating free carbon and Mg_2C_3, which upon hydrolysis gives methylacetylene. By all conceivable tests, Mg_2C_3 must be a pure substance. The concept that Mg_2C_3 contains a three-membered carbon chain in its crystal lattice appears to be correct.

2. Magnesium acetylide has been prepared from magnesium diethyl and acetylene.

3. An X-ray powder has been obtained of MgC_2. The data are compared with those expected for the tetragonal CaC_2 structure having the predicted axes $a_0 = 4.86$ Å., $c_0 = 5.76$ Å.

4. An explanation is proposed for the observed instability and reactivity of MgC_2.

BALTIMORE, MD.   RECEIVED NOVEMBER 19, 1942

Electric Moments of Ortho-substituted Phenols and Anisoles. I. Halogen Derivatives[1]

BY W. F. ANZILOTTI[2] AND B. COLUMBA CURRAN

Electric moments of ortho-substituted phenyl ethers are of interest in the study of the effects of steric hindrance between an alkoxy group and an ortho substituent on the configuration of these molecules. An analysis of the moments of the corresponding phenols permits a comparison of the extent and strength of intramolecular hydrogen bonding in these compounds. Interpretation of the observed moments of substituted phenols and anisoles must be based on values calculated for all possible configurations. These calculations require a knowledge of bond moments and of bond angles obtained from diffraction measurements. No diffraction data are available for alkyl phenyl ethers. The average oxygen valence angle reported from X-ray analy-

ses[3] of resorcinol crystals is about 117°. This deviation from the tetrahedral angle may be partly due to intermolecular hydrogen bonding. A value of 118° has been assigned[4] to the oxygen bond angle in di-p-iodophenyl ether from electron diffraction measurements on the vapor. From these data, and from a consideration of steric and resonance effects, the authors have assumed an oxygen valence angle of 115° in substituted phenols, and of 120° in substituted anisoles.

The ring-to-oxygen moment in these compounds cannot be evaluated directly. The corresponding moment in diphenyl ether may be calculated from the moment[5] of this compound in benzene,

(3) Robertson, Proc. Roy. Soc. (London), A157, 79 (1936); A167, 122 (1938).

(4) Maxwell, Hendricks and Mosley, J. Chem. Phys., 3, 699 (1935).

(5) Appendix Tables, Trans. Faraday Soc., 30, App. (1934). Unless otherwise indicated, electric moments in this paper are taken from this source, and are in Debye units.