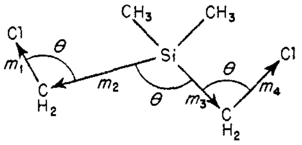
electron-drawing phenyl group will render the silicon electrons less available to the second. Second, structures involving double bond character of the Si–C_{arom} bonds will be sterically hindered because of the necessity of having both phenyl rings coplanar in the resonance hybrid representing the structures of this molecule.

The two other compounds whose dipole moments were measured in this study have to be treated in a special manner because their component moments act in a system involving free rotation of a complex chain of atoms. While the instantaneous value of the over-all moment changes the average value may be calculated by the equation of Eyring[18] developed by the technique of matrix algebra. This equation, with slightly modified notation, is

$$\bar{\mu}^2 = \sum_{j=1}^{n} m_j^2 + 2\sum_{j=1}^{n}\sum_{s>j}{}_{\text{k}}^{s-1} \cos \theta_{\text{k}} m_j m_s$$

where m_j is the value of the jth component moment, θ_k is the angle between the jth and the $(j + 1)$th moment vectors (considered to be 0° if the two moments are in the same direction), and the product $m_j m_s$ is considered negative if the direction of the two vectors is not the same along the line of atoms joining them.

In calculating the moments of the two compounds the component moments of the two methyl groups were not considered. The solution of the Eyring equation for bis-(chloromethyl)-dimethylsilane is

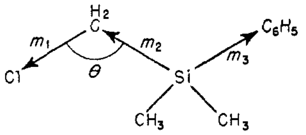


where $m_1 = m_4 = \mu_{\text{C-Cl}} = 1.93\ D$[1], $m_1 = m_3 = \mu_{\text{Si-C}} = 0.25\ D$,[1] and $\theta = 109° 28'$.

$$\bar{\mu}^2 = 2m_1{}^2 + 2m_2{}^2 - 2[m_1{}^2 \cos^3 \theta + m_2{}^2 \cos \theta - 2m_1 m_2 \cos \theta\,(1 + \cos \theta)]$$

Substitution of the numerical values leads to a calculated average value of 2.77 D, as compared to the observed value of 2.21 D. This great negative deviation may be attributed to electrostatic repulsion with a consequently lower moment than that calculated on the basis of free rotation. An analogous explanation was made by Smyth and Walls[19] in comparing the calculated (2.42 D) and observed (2.07 D) moments of 1,3-dichloropropane.

For chloromethyldimethylphenylsilane, it would be predicted that the electrostatic repulsion would not be as strong between the chlorine atom and the phenyl group as between the two chlorine atoms. This should result in much lower hindrance to free rotation, and consequently better agreement between calculated and observed values. For chloromethyldimethylphenylsilane the solution to Eyring's equation is



where $m_1 = \mu_{\text{C-Cl}} = 1.93\ D$, $m_2 = \mu_{\text{Si-C aliph}} = 0.25\ D$, $m_3 = \mu_{\text{Si-C arom}} = 0.42\ D$, $\theta = 109° 28'$.

$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 - 2[(m_1 m_2 - m_2 m_3)\cos \theta + m_1 m_3 \cos^2 \theta]$$

Upon substitution, the average moment value is calculated to be 2.01 D which, as expected, is in much better agreement with the observed value, 1.93 D, than was found in the case of the bis-(chloromethyl)-dimethylsilane.

PITTSBURGH 13, PENNSYLVANIA

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[18] H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[19] C. P. Smyth and W. S. Walls, THIS JOURNAL, **54**, 2261 (1932).

[CONTRIBUTION NO. 878 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Electron Moments and Structures of Organosilicon Compounds. III. The Oxygen–Silicon Bond[1,2]

BY HENRY FREISER, MARY V. EAGLE AND JOHN SPEIER

RECEIVED AUGUST 29, 1952

The dielectric constants and densities of benzene solutions of ethoxytrimethylsilane, hexamethyldisiloxane, ethoxytriphenylsilane, chloromethylethoxydimethylsilane, diethoxydimethylsilane and ethoxydimethylphenylsilane have been determined at 30.0°. The dipole moment values of these compounds have been calculated as 1.18, 0.79, 1.25, 2.14, 1.36 and 1.30 D, respectively. The results are consistent with an assumed Si–O–Si bond angle of 131° in hexamethyldisiloxane. The effect of the Si–O link upon the Si–carbon bond moment is seen to be quite large, as might be predicted from the electronegative character of oxygen.

In previous papers in this series[1,3] the ease with which silicon is electrically distorted was noted. In the present report, the extension of the study to compounds in which silicon is bonded to the highly electronegative oxygen atom is discussed. The effects noted with various organosilicon compounds are more pronounced when silicon–oxygen bonds are involved.

Experimental

Preparation and Purification of Materials. Ethoxytrimethylsilane was prepared from chlorotrimethylsilane and absolute alcohol. The product was distilled twice, the second time through a column of about 50 plates. The fraction used had the properties: b.p. 74° at 736 mm., n^{25}_{D} 1.3712, d^{25}_{4} 0.7521; sp. ref. 0.3016; calcd. sp. ref. 0.3018. Sauer[4] reported b.p. 75° at 745 mm., n^{20}_{D} 1.3743, d^{20}_{4} 0.7573.

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[1] Paper II, THIS JOURNAL, **75**, 2821 (1953).

[2] Abstracted from the thesis of M. V. E. submitted in partial fulfillment of the requirements of the M.S. degree in Chemistry, Summer, 1952.

[3] Paper I, *ibid.*, **73**, 5229 (1951).

[4] R. O. Sauer, *ibid.*, **66**, 1707 (1944).

Hexamethyldisiloxane.—Hexamethyldisiloxane was prepared by hydrolysis of chlorotrimethylsilane. The product was carefully distilled. Only the center 65 ml. of a 400 ml. plateau was used although the entire plateau had the properties: b.p. 100.8° at 743 mm., n^{25}_{D} 1.3741, d^{25}_{4} 0.7580; sp. ref. 0.3013, calcd. sp. ref. 0.3015. Burkhard, *et al.*, report[5] b.p. 100.5°, n^{20}_{D} 1.3774, d^{20}_{4} 0.7619.

Ethoxytriphenylsilane.—Dichlorodiphenylsilane (379 g., 1.5 moles) was added to the ether solution of phenylmagnesium bromide prepared from 251 g., 1.6 moles of bromobenzene. The mixture was heated to 85° as the ether was removed to leave a hard white mass of solids. The ether was returned to the solids and stirred up into a slurry. The slurry was filtered. To the filtrate 69 g., 1.5 moles of alcohol and 118 g., 1.5 moles of pyridine was added. After about 18 hours, this mixture was filtered free of pyridine hydrochloride and distilled to yield 193 g., 43% over-all yield, of ethoxytrimethylsilane, b.p. 229° at 18 mm., m.p. 60–63°. Recrystallized from ligroin this melted at 63–64°.

Anal. Si, 9.53. Calcd. for $C_{20}H_{20}OSi$: Si, 9.22.

(Chloromethyl)-ethoxydimethylsilane was prepared by slowly adding 466 g., (10 moles) of absolute alcohol below the surface of 1432 g., 10 moles, of refluxing chloromethyldimethylchlorosilane. Refluxing was continued four hours before the product was distilled. A considerable amount of the unreacted reagents was recovered followed by 630 g., 42%, of (chloromethyl)-ethoxydimethylsilane, b.p. 132° at 741 mm., n^{25}_{D} 1.4124, d^{25}_{4} 0.9438; sp. ref. 0.2638, calcd. sp. ref. 0.2653; and 220 g., 19%, of 1,3-bis-dichloromethyltetramethyldisiloxane.

Anal. Calcd. for $C_5H_{13}OClSi$: Si, 18.38. Found: Si, 18.40.

Diethoxydimethylsilane was carefully redistilled commercial material, b.p. 112° at 741 mm., n^{25}_{D} 1.3793, d^{25}_{4} 0.8344; sp. ref. 0.2772, calcd. sp. ref. 0.2770; reported[6] b.p. 114° at 740 mm., d^{25}_{4} 0.830.

Ethoxydimethylphenylsilane was prepared from chlorodimethylphenylsilane and absolute alcohol in the presence of pyridine in chloroform solution. Pyridine hydrochloride was precipitated by dilution of the mixture with benzene. The product was filtered and distilled to give a yield of 75% ethoxydimethylphenylsilane, b.p. about 93° at 25 mm., n^{25}_{D} 1.4799, d^{25}_{4} 0.9263; sp. ref. 0.3066, sp. ref. calcd. 0.3078.

Anal. Found: Si, 15.38, 15.47. Calcd.: Si, 15.21.

Measurements and Calculations.—The procedure used has been described previously.[7] The measurements are summarized in Table I where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction f_2 of the substance indicated are given as well as the molar polarization and molar refraction. The table also includes the polarization obtained by extrapolation to $f_2 = 0$ of the P_2 values and the dipole moment, μ, calculated therefrom in the usual manner.

Discussion of Results

The dipole moment observed for ethoxytrimethylsilane, 1.18 *D*, can be considered as the resultant of the $(CH_3)_3Si–O$ and the $O–C_2H_5$ group moments. The value of the latter group moment can be calculated from the dipole moment value of ethyl ether, 1.27 *D*,[8] and the value of the C–O–C bond angle, 111°, as observed in methyl ether. From the value of the $C_2H_5–O$ group moment thus calculated, 1.12 *D*, the value of the $(CH_3)_3Si–O$ group moment of 0.95 *D* is found, assuming the Si–O–C bond angle to be 111°. The 0.95 *D* value of the $(CH_3)_3Si–O$ group is thus the highest found for any group in which $(CH_3)_3Si–$ occurs. This suggests that one of the reasons for the great stability of the Si–O bond is the great difference in electronegativity of the two atoms.

Table I

Dielectric Polarization Data at 30.0°

f_2	ϵ	d	P_2
Ethoxytrimethylsilane, $MR_D = 35.6$, $\mu = 1.18$ *D*			
0.00000	2.2627	0.86823	(63.87)
.02216	2.2885	.86392	63.87
.03373	2.3014	.86171	63.71
.04233	2.3120	.86012	64.01
Hexamethyldisiloxane, $MR_D = 48.9$, $\mu = 0.79$ *D*			
0.00000	2.2627	0.86823	(61.4)
.05418	2.2564	.85520	61.5
.05515	2.2567	.85594	61.0
.07461	2.2558	.85063	61.9
.09352	2.2516	.84750	61.1
Ethoxytriphenylsilane, $MR_D = 96.8$, $\mu = 1.25$ *D*			
0.00000	2.2627	0.86823	(128.0)
.005275	2.2784	.87176	127.5
.01055	2.2936	.87534	126.9
.01958	2.3217	.88079	129.4
.02994	2.3495	.88701	128.3
Chloromethylethoxydimethylsilane, $MR_D = 40.3$, $\mu = 2.14$ *D*			
0.00000	2.2627	0.86823	(132.8)
.01237	2.3330	.86982	132.0
.01944	2.3796	.87072	136.4
.03391	2.4567	.87244	131.7
.04266	2.5034	.87350	131.0
Diethoxydimethylsilane, $MR_D = 41.1$, $\mu = 1.36$ *D*			
0.00000	2.2627	0.86823	(78.5)
.01132	2.2813	.86752	77.1
.02051	2.2982	.86684	78.7
.03113	2.3155	.86614	78.4
.04241	2.3382	.86536	79.8
Ethoxydimethylphenylsilane, $MR_D = 55.2$, $\mu = 1.30$ *D*			
0.00000	2.2627	0.86823	(89.3)
.02232	2.3097	.87069	89.8
.03518	2.3343	.87221	89.0
.04591	2.3557	.87314	89.1

Using the value of the $(CH_3)_3Si–O$ group moment of 0.95 *D* and assuming that the value of 111° for the bond angle C–O–C is also correct for the bond angle Si–O–Si, one can calculate the dipole moment of hexamethyldisiloxane as being 1.08 *D*. The observed moment of this compound, 0.79 *D*, is considerably lower than the calculated value. This can only be explained upon the widening of the bond angle because of the presence of the bulky trimethylsilyl groups. If the bond angle Si–O–Si were assumed to be 131°, exact correspondence of observed and calculated moment values could be obtained. Earlier dipole work by Sauer[9] led to the assumption of this widening, which was estimated by him to result in a bond angle of 160°.

Our result is in excellent agreement with a value of the O–Si–O bond angle of 130 ± 10° determined from X-ray studies on the cyclic octasiloxane and on frozen stretched silicone rubber by Dr. L. K. Frevel.[10]

A comparison of the moments of ethoxytrimethylsilane and ethoxytriphenylsilane is very interesting.

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(5) C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 97 (1947).

(6) R. R. McGregor and E. L. Warrick, U. S. Patent 2,380,057.

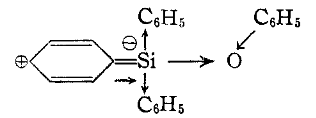
(7) R. K. Keswani and H. Freiser, This Journal, **71**, 218 (1949).

(8) O. Hassel and A. H. Uhl, *Z. physik. Chem.*, **B8**, 187 (1930).

(9) R. O. Sauer and P. J. Mead, This Journal, **68**, 1794 (1946).

(10) Quoted in P. J. Flory, L. Mandelkern, J. B. Kinsinger and W. B. Schultz, *ibid.*, **74**, 3364 (1952).

The comparatively small increase in the dipole moment in the latter (its value is 1.25 *D*) does not sufficiently indicate the great difference between the two compounds. For in ethoxytriphenylsilane, the moment can be explained only if the three phenyl nuclei are assumed to donate electrons to the silicon to an extent to cause a C_6H_5–Si moment of −0.14 *D*, that is, having the positive end of the dipole toward the ring and the negative end toward silicon. This calculation is based upon the assumption that the Si–O–C bond angle is 111°, as was assumed for ethoxytrimethylsilane. If the angle were wider, the contribution of electrons from the phenyl groups would have to be ever larger to account for the observed moment. This is then seen to be another example of the "reverse halogen" effect

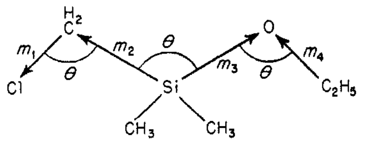


It may be surmised that the effect would be stronger in this compound were it not for the fact that the bulky phenyl groups sterically interfere with each other and hinder the full play of the resonance interaction which requires planarity. This will be discussed further in connection with the moment of ethoxydimethylphenylsilane.

The component moments of the remainder of the compounds act in molecular systems involving free rotation of a complex chain of linked atoms. The over-all moments of these compounds can be calculated by the method of Eyring[11] referred to previously.[1]

In considering the compound chloromethylethoxydimethylsilane, it might be predicted that there should be a significant negative deviation from the calculated to the observed value of the dipole moment. The high electronegativity of both oxygen and chlorine might cause rather strong repulsion between the chlorine atom and the ethoxy group, perhaps almost as strong as that between the two chlorine atoms in bis-(chloromethyl)-dimethylsilane.[1]

The equation for the calculation of the moment of this compound is

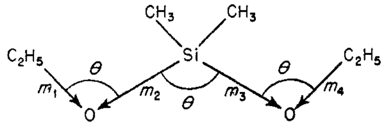


$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 + m_4^2 + 2[-m_1m_4\cos^3\theta + (m_2m_4 - m_1m_3)\cos^2\theta + (m_2m_3 + m_3m_4 - m_1m_2)\cos\theta]$$

If the tetrahedral angle be assumed to occur throughout the compound, then substitution of the values $m_1 = 1.93$ *D*, $m_2 = 0.25$ *D*, $m_3 = 0.95$ *D*, $m_4 = 1.12$ *D*, and $\theta = 109° 28'$ results in a moment for chloromethylethoxydimethylsilane of 2.28 *D*. The observed value is 2.14 *D*; the difference, 0.14 *D*, is not as large as expected on the basis of the electrostatic repulsion of chlorine and oxygen. The alkyl group may modify the electronegativity of oxygen. Furthermore, electrostatic repulsion of the chlorine and oxygen does not interfere with the free rotation of the O–C_2H_5 group.

If it be true that the repulsion between the chlorine and the ethoxy group is slight, as indicated above, then, in spite of the high electronegativity of the two oxygen atoms, it would be predicted that for diethoxydimethylsilane, there will be only small deviation between the observed and the calculated values of the moment, unless there is significant widening of the O–Si–O bond angle.

The specific equation for this compound is

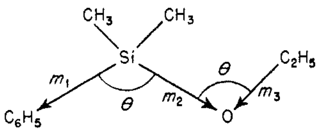


$$\bar{\mu}^2 = 2m_1^2 + 2m_2^2 + 2[m_1^2\cos^3\theta + 2m_1m_2\cos^2\theta + (m_2^2 + 2m_1m_2)\cos\theta]$$

and when $m_1 = m_4 = 1.12$ *D*, $m_2 = m_3 = 0.95$ *D*, and θ is assumed to be 109° 28′ throughout, a value of 1.63 *D* is obtained for the moment of diethoxydimethylsilane. This is in surprising lack of agreement with the observed value of 1.36 *D*.

It has already been observed that there is little interaction and consequent lowering of the moment between the chloromethyl and ethoxy groups. It would therefore be predicted that in the compound ethoxydimethylphenylsilane there will be but slight hindrance of free rotation, and the observed value of the moment should not be much lower than the calculated value.

The Eyring equation for this compound is



$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 + 2\,m_1m_3\cos^2\theta + (m_1m_2 + m_2m_3)\cos\theta$$

The values $m_1 = 0.42$ *D*, $m_2 = 0.95$ *D*, $m_3 = 1.12$ *D*, and $\theta = 109° 28'$ throughout, yield a dipole moment value for ethoxydimethylphenylsilane of 1.21 *D*. Since the observed value of 1.30 *D* is higher than the calculated value, there can be no question of explaining the difference between them by postulating hindrance of free rotation; the explanation must be sought elsewhere. It is possible that the assumptions regarding the value of either the bond angle or the bond moments may be in error. In view of the highly polarizable nature of the Si–C_{arom} bond, which has been demonstrated previously by the wide range of moment values which it assumed, it seems reasonable that this bond moment is the one most in error. If it be assumed that the bond angles are nearly correct, and the values for the moments of the Si–O and the O–C_2H_5 bonds are valid, then use of the observed compound moment of 1.30 *D* yields for the Si–C_{arom} bond moment a value of −0.33 *D*, with the positive end of the dipole toward the ring carbon. This situation might be explained by the large contribution of resonance structures such as

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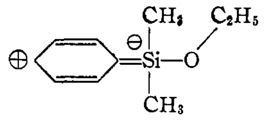
(11) H. Eyring, *Phys. Rev.*, **39**, 746 (1932).



The value of −0.33 *D* for the moment of the Si–C_{arom} bond is not altogether improbable in the light of discussions of previous compounds, since there is evidence to indicate that this bond has a value of at least −0.14 *D*, with the negative end toward silicon, in the compound ethoxytriphenylsilane. The presence of a highly electronegative element such as oxygen, attached to the central silicon atom, seemingly should promote such structures. It would seem, however, that the chloromethyl group attached to silicon should also promote "reverse halogen" structures. Yet use of the value +0.42 *D*, with the negative end of the dipole toward the ring carbon, permitted, in the case of chloromethyldimethylphenylsilane, calculation of a value very close to the observed value.[1] That replacement of the chloromethyl group by the ethoxy group, leaving the dimethylphenylsilyl residue unchanged could result in a change of the Si–C_{arom} bond moment from +0.42 to −0.33 *D*, a total change of 0.75 *D*, is difficult to understand.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY, UNION CARBIDE AND CARBON CORPORATION]

The Vapor Pressure and Critical Constants of Uranium Hexafluoride[1]

BY GEORGE D. OLIVER,[2] H. T. MILTON AND J. W. GRISARD

RECEIVED JANUARY 5, 1953

Vapor pressure measurements were made on uranium hexafluoride from 0° to the critical point. The vapor pressure of the solid is represented by the equation: $\log_{10}P_{mm} = 6.38363 + 0.0075377t - 942.76/(t + 183.416)$. Pressure data on the liquid from 64 to 116° are represented by equation (2): $\log_{10}P_{mm} = 6.99464 - 1126.288/(t + 221.963)$, and above 116° by equation (3): $\log_{10}P_{mm} = 7.69069 - 1683.165/(t + 302.148)$. Critical constants determined from experimental data are: t_c, 230.2 ± 0.2° and P_c, 45.5 ± 0.5 atm. Calculated ΔH_v at the triple point, 64.02 ± 0.05°, was 6.82 kcal./mole. Calculated deviations from ideality were 0.0062 at 25° and 0.043 at 64.02°.

Since the early vapor pressure data of Ruff and Heinzelmann, in 1911, many measurements on uranium hexafluoride have been made by various methods in the low pressure range. However, there is only one report of an attempt to measure the vapor pressure above four atmospheres. Most of these data are summarized along with other properties of uranium hexafluoride in reference 3. Uncertainties in the published data, which were due indirectly to the reactivity of the compound, have been essentially eliminated in the present work by an ebulliometric method of measurement.

Several values for the critical temperature and pressure of this compound have been estimated from related physical properties.[3] Since these values vary as much as 30° and 20 atm., respectively, it was considered worthwhile to publish experimental values for these constants.

Experimental

Material.—Two samples of uranium hexafluoride were used in the present investigation over the entire liquid range. The purity of these samples was estimated to be 99.75 mole per cent. by mass spectra analysis that showed 0.01% fluorocarbon and 0.24% other volatiles, and emission spectra that showed 0.005% non-volatile impurities. The vapor pressure of a third sample was measured over the solid range and up to 2500 mm. of the liquid range. Volatile impurities were removed from this sample by repeatedly pumping the equilibrated vapors from the sample, held at room temperature, until only one-fourth of the original material remained. Then, the residue was treated with anhydrous potassium fluoride for 68 hours. The purity of the final material was 99.985 mole per cent., as determined by a calorimetric fractional melting point method. The data indicated that a final elimination of volatile impurities, *e.g.*, hydrogen fluoride, was accomplished in the boiler of the vapor pressure apparatus.

Apparatus and Procedure.—Both the ebulliometric and static apparatuses were used to measure the vapor pressure of the solid, while only ebulliometric measurements were made on the liquid. Primary equipment employed in the static measurements on the solid state consisted of the manometer and platinum resistance thermometer for the ebulliometric apparatus, a refrigerated 20-gallon bath, and a null-point pressure transmitter. The transmitter was connected between the manometer system containing helium and a nickel cylinder containing 15 g. of uranium hexafluoride. The cylinder and thermometer were mounted adjacently in a copper block which was suspended in the bath. Temperature of the bath was regulated to ±0.005°. Measurements of the vapor pressure were verified by pumping off the vapor above the valve on the sample cylinder and remeasuring the pressure of new charges of vapor until reproducible pressures were obtained.

Two ebulliometers were used to measure the vapor pressure of the liquid and a portion of the sublimation pressures. The low pressure apparatus has been described briefly,[4] and both are described in detail in a pending publication.[5] Briefly, the high pressure apparatus consisted of two monel boiling point tubes connected through traps to a common pressure system containing helium as a buffer. A certified platinum resistance thermometer measured the boiling temperatures of the material in each tube. The pressure in the system was determined by measuring the boiling temperature of water in one boiling point tube and obtaining the corresponding pressure from steam tables.[6] Temperatures were measured absolutely to within ±0.01° but the accuracy of the pressure readings was no better than that of the steam tables.

To determine the critical temperature and pressure, the system was brought to equilibrium at a temperature and pressure below the critical point of uranium hexafluoride. The heat input to the system was maintained practically

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(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) Monsanto Chemical Co., Texas City, Texas.

(3) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Part I, National Nuclear Energy Series, Division VIII, Volume 5, McGraw-Hill Book Co., Inc., 1951, p. 404.

(4) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

(5) G. D. Oliver and J. W. Grisard, *Rev. Sci. Instruments*, in press.

(6) N. A. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).