The limiting conductances were also evaluated by the mathematical extrapolation of the curves for Λ *vs.* $\sqrt{c}$. The method of least squares applied to the data for dilute solutions gave the following values for the limiting conductances

Salt	Λ_0	Slope	Theor. slope
KIO_4	127.92	−94.08	−89.61
$KReO_4$	128.20	−97.08	−89.68

The extrapolated value obtained by Pushin and Tutundzie[1] was 125.7 for potassium perrhenate.

The data were also plotted according to a method proposed by Shedlovsky[6] in which an extrapolation function of the form $1/\Lambda = (1/\Lambda_0) + k\sqrt{c}$ is used. The data for solutions more dilute than 0.01 molar fell on straight lines and yielded values of Λ_0 of 127.95 for potassium metaperiodate and 128.25 for potassium perrhenate. These values are somewhat higher than those obtained by either of the other two methods but the extrapolation is rather long and steep. The agreement between the various methods of evaluating Λ_0 is considered satisfactory. The values accepted for Λ_0 are 127.90 for the metaperiodate and 128.20 for the perrhenate. These are believed accurate to within ±0.07 conductance unit.

Mobilities of the Anions.—Since the mobility of the potassium ion at infinite dilution and 25° is well known (73.52 on the Jones and Bradshaw[3] standard), it is possible to calculate the mobilities of the metaperiodate ion and the perrhenate ion using the limiting conductances of the potassium salts measured in this investigation. This would yield the following values: metaperiodate ion, 54.38 ± 0.07 and perrhenate ion, 54.68 ± 0.07.

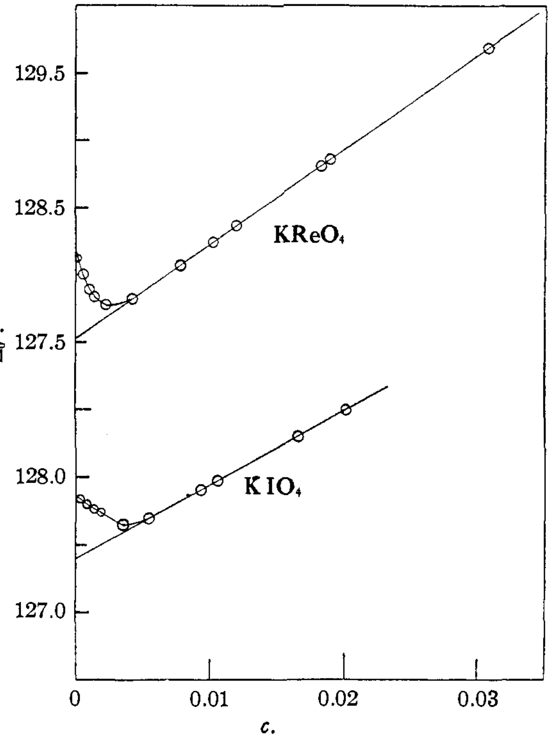

Fig. 1.—Plots of Shedlovsky function.

Summary

The electrical conductances of aqueous solutions of potassium metaperiodate and potassium perrhenate were measured over the concentration range 0.0004 *m* to approximate saturation.

The limiting conductances were determined by three independent methods with satisfactory agreement.

The densities of the solutions were determined with an accuracy of approximately 1 part in 15,000.

The limiting conductances of the anions were determined using the recorded value for the potassium ion and the measured values for the salts from this investigation.

BLOOMINGTON, INDIANA RECEIVED NOVEMBER 30, 1945

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[6] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. IV. Amines

BY ROBERT O. SAUER AND R. H. HASEK[1]

In the first paper[2] of this series which described the hydrolysis and alcoholysis products of trimethylchlorosilane attention was directed toward the unstable nature of trimethylsilanol as compared with triethylsilanol and its higher homologs. We now report a parallel study of the ammonolysis and aminolysis products of this chlorosilane.

Stock and Somieski[3] treated chlorosilane vapor with ammonia and isolated the tertiary amine $(H_3Si)_3N$, b. p. 52°. With excess ammonia presence of the primary and secondary amines was assumed; neither, however, was isolated. Aminosilane presumably condensed with itself producing ammonia and disilazine, $H_3SiNHSiH_3$; the latter decomposed slowly with the formation of silane and the non-volatile polysilazine, $(H_2SiNH)_x$. Chlorosilane with methylamine and with ethylamine yielded[4] N-methyldisilazine, b. p. 32°, and N-ethyldisilazine, b. p. 66°, respectively.

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[1] Present address: Tennessee Eastman Corp., Kingsport, Tenn.

[2] Sauer, THIS JOURNAL, **66**, 1707 (1944).

[3] Stock and Somieski, *Ber.*, **54**, 740 (1921).

[4] Emeleus and Miller, *Nature*, **142**, 996 (1938); *J. Chem. Soc.*, 819 (1939).

In our experiments trimethylchlorosilane has given only one ammonolysis product, hexamethyldisilazine.[2] Under similar conditions we obtained triethylaminosilane and hexaethyldisilazine[5] from triethylchlorosilane. Hence, it appears that the stability of the R_3SiNH_2 compounds is of about the same order as that of their R_3SiOH analogs. Ready elimination of ammonia or water (yielding the disilazine or disiloxane, respectively) appears to characterize the lower members of both series.

Hexamethyldisilazine was found unexpectedly stable to attack at the nitrogen–hydrogen bond. Although an 88–94% yield of methane is obtained[2] in the Zerewitinoff determination (equation 1), no reaction was observed with metallic sodium at 125° after sixteen hours. Neither did this amine discharge the blue color of sodium dissolved in liquid ammonia. Another indication of the inertness of the nitrogen–hydrogen bond was our failure to isolate from the ammonolysis of trimethylchlorosilane the tertiary amine, $[(CH_3)_3Si]_3N$, a compound which appears sterically possible by inspection of Fisher–Hirschfelder models and chemically probable in the light of Stock's results. This point was checked by our inability to effect a reaction between purified hexamethyldisilazine and trimethylchlorosilane (or silicon tetrachloride) at about 60°.

$$(CH_3)_3SiNHSi(CH_3)_3 + CH_3MgI \longrightarrow CH_4 + [(CH_3)_3Si]_2N\text{-}MgI \quad (1)$$

With methylamine trimethylchlorosilane yields trimethyl-N-methylaminosilane, b. p. 71°, which upon further treatment with the chlorosilane yields heptamethyldisilazine (equation 2).

$$3(CH_3)_3SiNHCH_3 + (CH_3)_3SiCl \longrightarrow 2[(CH_3)_3Si]_2NCH_3 + CH_3NH_2{\cdot}HCl \quad (2)$$

The significant stages in the reaction appear to be represented by

$$(CH_3)_3SiNHCH_3 + (CH_3)_3SiCl \rightleftarrows [(CH_3)_3Si]_2NCH_3 + HCl \quad (3a)$$

$$(CH_3)_3SiNHCH_3 + 2HCl \longrightarrow (CH_3)_3SiCl + CH_3NH_2{\cdot}HCl \quad (3b)$$

Two factors may suppress the analogous sequence of reactions with hexamethyldisilazine; either the formation of hydrogen chloride is blocked by the "inertness" of the hydrogen attached to nitrogen, or else the degradative cleavage by hydrogen chloride in the sense of equation 3b does not proceed. The latter factor is precluded by the demonstration that hydrogen chloride (in accordance with the generalization of Stock[3]) readily cleaved hexamethyldisilazine.

The hydrolysis of hexamethyldisilazine is unusual in several respects. As noted earlier[2] it is cleaved quantitatively by dilute acids, giving ammonium salts and the silanol (as the primary product). However, the compound is remarkably resistant to hydrolysis by boiling water or dilute alkalies. Such behavior is apparently a consequence of its water insolubility, for upon addition of methanol to the amine–water mixture a homogeneous solution results accompanied by vigorous hydrolysis of the compound.

In addition to the aminosilanes noted above we have prepared impure trimethyl-N-ethylaminosilane, b. p. 90°, and trimethyl-N,N-diethylaminosilane, b. p. 126°.

We have based our assigned structural formulas for the four new compounds prepared from trimethylchlorosilane on the method of synthesis and on the recognized stability of the carbon–silicon and carbon–nitrogen bonds under the conditions of synthesis and isolation. Determination of neutral equivalents was used to confirm the composition of the expected products. The only product isolated from the reaction of trimethylchlorosilane and ammonia was hexamethyldisilazine, although one might predict *a priori* that three are possible. The structure assigned to this product was confirmed by elementary analyses for carbon, hydrogen, silicon and nitrogen and further supported by satisfactory neutral equivalent and "active hydrogen" determinations.[2] From trimethylchlorosilane and methylamine only two silicon-containing products can result assuming inviolability of carbon–silicon, carbon–nitrogen and carbon–hydrogen bonds; neutral equivalents on the two products obtained confirmed our expectations. From diethylamine and trimethylchlorosilane one predicts (on the assumptions listed above) only a single product, trimethyl-N,N-diethylaminosilane. The neutral equivalent of the product found indicated that the expected structure was obtained. The structure of the compound from trimethylchlorosilane and ethylamine was assigned primarily on the basis of the yield of trimethyl-N-methylaminosilane obtained in the reaction with methylamine. The neutral equivalents on our product, trimethyl-N-ethylaminosilane, indicated the presence of appreciable inert impurity.

Experimental

Method of Analysis.—All neutral equivalents reported in this experimental part with the exception of those on the triethylsilyl derivatives were obtained by adding the sample to excess 0.1 *N* hydrochloric acid. After vigorous shaking the excess acid was back-titrated with 0.1 *N* sodium hydroxide solution to the methyl orange end-point.

Trimethylsilyl Derivatives

Hexamethyldisilazine.—(a) Preparation of this substance was carried out in ethereal solution as previously described.[2] It was noted that care must be taken to keep the reaction mixture anhydrous. In one experiment in which water was added to the reaction mixture to dissolve the ammonium chloride hydrolysis of the amine resulted, yielding trimethylsilanol and hexamethyldisiloxane. Our

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(5) Kraus and Nelson (This Journal, **56**, 195 (1934)) report the preparation of this compound by the reaction of potassium amide in liquid ammonia with triethylsilane, followed by neutralization of the potassium salt with ammonium bromide. Their yield of $[(C_2H_5)_3Si]_2N\text{-}K$ was nearly quantitative indicating the condensation

$$2(C_2H_5)_3SiNH^- \longrightarrow [(C_2H_5)_3Si]_2N^- + NH_2^-$$

under the conditions of their experiment.

product had the following properties: b. p. 125.7–126.2° (758 mm.); $n^{20}\mathrm{D}$ 1.4078; d^{20}_4 (vac.) 0.7741; neut. equiv. 160.2, 160.5 (theory, 161.3).

(b) **Reaction of Trimethylchlorosilane with Liquid Ammonia.**—A 2-liter unsilvered Dewar flask was provided with a cork stopper, a stirrer and an addition funnel with a 5-mm. capillary tube extending about four inches below the liquid surface. Trimethylchlorosilane (296 g., 2.73 moles) was added to 900 ml. of liquid ammonia with vigorous stirring over a period of three and three-quarters hours. The ammonia-insoluble hexamethyldisilazine separated as a lower layer. After most of the ammonia had been removed by distillation the residual sludge was distilled until ammonium chloride began to sublime. The residue was cooled and the ammonium chloride dissolved in 450 ml. of water. The upper layer was then separated, dried over sodium sulfate and combined with the previous distillate. Distillation gave 30 ml. boiling in the range 95–125° (mostly trimethylsilanol and hexamethyldisiloxane) and a total of 99 g. (45%) of hexamethyldisilazine, b. p. 125.2–125.7°, $n^{20}\mathrm{D}$ 1.4081.

Attempt to Detect Trimethylaminosilane in the Ammonolysis Product.—As none of the earlier experiments had afforded any indication of the presence of trimethylaminosilane (estimated b. p. 50–80°) and since a large excess of ammonia and low temperatures should favor its formation, an ammonolysis was run at Dry Ice–acetone temperature. A 750-ml. test-tube charged with 500 ml. of liquid ammonia and provided with a cork stopper, a stirrer and a dropping funnel with a capillary extension reaching below the liquid surface was immersed in a Dry Ice–acetone bath. Stirring was begun and 111.5 g. (1.03 moles) of trimethylchlorosilane was added rapidly over a fifteen-minute period. The ammonia was then slowly distilled through two traps immersed in ice. A few milliliters of liquid was collected in the first trap and a single drop in the second. The ammonium chloride and hexamethyldisilazine left in the test-tube were extracted with two portions, totalling 350 ml., of dry toluene. This toluene extract and the small amount of liquid collected in the ice traps were combined and fractionally distilled. Only 10 ml. of liquid, b. p. 79.4–105.6°, was collected. No indication of even a small amount of reasonably pure primary amine was obtained.

A similar experiment was performed to determine the nature of the solid material formed in the reaction. One mole of trimethylchlorosilane was added to excess liquid ammonia at −70°. The ammonia was then slowly distilled, the last traces being removed by heating to 60–70° under 15–60 mm. pressure. The disilazine was then completely removed from the solid residue by a further period of exhaustion at 0.1 mm.; 37 g. (46%) of hexamethyldisilazine was so distilled at room temperature, 54 g. (calcd. for ammonium chloride, 53.5 g.) of white solid remaining. A Volhard chlorine analysis showed this residue to be essentially pure ammonium chloride.

Anal. Calcd. for NH_4Cl: Cl, 66.28. Found: Cl, 65.82.

Trimethyl-N-methylaminosilane.—(a) This compound was prepared in ethereal solution as described for hexamethyldisilazine, using an excess of anhydrous methylamine. From 54 g. (0.50 mole) of trimethylchlorosilane in 500 ml. of ether there was obtained 19.7 g. (38%) of trimethyl-N-methylaminosilane, b. p. 71° (755 mm.), $n^{20}\mathrm{D}$ 1.3905, d^{20}_4 (vac.) 0.7395; appreciable hexamethyldisiloxane (12.7 g.) was also found.

Anal. Calcd. for $C_4H_{13}SiN$: neut. equiv., 103.2. Found: neut. equiv., 106.2, 105.0.

(b) To 200 ml. of anhydrous liquid methylamine in the same apparatus described in Part (b) under hexamethyldisilazine was added 217 g. (2.0 moles) of trimethylchlorosilane. After roughly half of the chlorosilane had been added the reaction mixture solidified. Upon completion of the addition the solid was broken up, shaken with ether and filtered by suction. The filtrate was fractionally distilled giving 114.5 g. (55%) of trimethyl-N-methylaminosilane, b. p. 70.0–70.6 (747 mm.), $n^{20}\mathrm{D}$ 1.3897, and about 20 g. of hexamethyldisiloxane. The residue from the distillation weighed 13.5 g. and consisted of crude heptamethyldisilazine (see below).

The residue from the filtration was exhausted to a pressure of 0.1 mm. giving a dry white solid weighing 130.5 g. (required for 2.0 moles $CH_3NH_2\cdot HCl$, 135 g.).

Trimethyl-N-ethylaminosilane.—Trimethylchlorosilane (108.5 g., 1.0 mole) in 500 ml. of absolute ether was added to an ice-cold solution of 100 g. of ethylamine in 500 ml. of absolute ether. On working up in the usual manner there was obtained 29.2 g. (25%) of trimethyl-N-ethylaminosilane, b. p. 90.1–90.8°, $n^{20}\mathrm{D}$ 1.3912, appreciably contaminated with an inert impurity, presumably azeotropic trimethylsilanol-hexamethyl-disiloxane,[2] b. p. 90.6°.

Anal. Calcd. for $C_5H_{15}SiN$: neut. equiv., 117.2. Found: neut. equiv., 125.2, 127.1.

Trimethyl-N,N-diethylaminosilane.—Trimethylchlorosilane (54 g., 0.5 mole) in 500 ml. of absolute ether was added to a solution of 80 g. of diethylamine (b. p. 55.1–55.4° at 750 mm.) in 1000 ml. of absolute ether. The yield of trimethyl-N,N-diethylaminosilane, b. p. 126.1–126.4° (750 mm.), $n^{20}\mathrm{D}$ 1.4112, was 20.4 g. (28%); 10.5 g. of hexamethyldisiloxane was also obtained.

Anal. Calcd. for $C_7H_{19}SiN$: neut. equiv., 145.3. Found: neut. equiv., 145.1, 145.2.

Reactions of Hexamethyldisilazine

Hydrolysis.—Under neutral or slightly basic conditions hydrolysis can yield trimethylsilanol.[2]

(a) Hexamethyldisilazine (25.7 g.) was refluxed for four hours with 50 ml. of distilled water. After cooling the upper layer was separated, dried briefly over anhydrous potassium carbonate and carefully distilled: Fraction A, b. p. 90.9–124.0°, 3.3 g.; Fraction B, b. p. 124.0–125.6°, 17.3 g.; residue, 2.6 g. Of Fraction A only 2.1 g. distilled below 100°; hence, the extent of hydrolysis under these conditions was about 10%.

The entire material was then refluxed with 100 ml. of 5% hydrochloric acid for one and one-half hours. No amine or trimethylsilanol odor was then detectable and the oily layer yielded 17.2 g. of hexamethyldisiloxane, $n^{20}\mathrm{D}$ 1.3775.

(b) Two grams of hexamethyldisilazine, $n^{20}\mathrm{D}$ 1.4078, and 18 ml. of 10% sodium hydroxide solution were refluxed for five hours. The oily layer was cooled, separated and dried over sodium sulfate. The refractive index, $n^{20}\mathrm{D}$ 1.4063, indicated that the extent of hydrolysis was about 5%. The results of this experiment encouraged the hope that acylation by means of the Schotten–Baumann reaction might be possible. However, with benzoyl chloride and 10% aqueous sodium hydroxide the only crystalline product was benzamide (m. p. and mixed m. p. 125–127°).

(c) Methanol was added in 10-ml. portions with gentle agitation to a mixture of 10 ml. of water and 35.3 g. of hexamethyldisilazine. The mixture gradually became warm and a strong odor of ammonia was apparent. After 40 ml. of methanol had been added the mixture became homogeneous and vigorous ebullition ensued. Upon cooling the characteristic odor of trimethylsilanol was noted.

Treatment with Sodium.—A mixture of 50 g. of hexamethyldisilazine and 1 g. of sodium was refluxed for sixteen hours. The surface of the molten sodium remained bright and apparently unaffected throughout this reflux period. In a second experiment the blue color produced by the solution of 4.5 g. of sodium in 1200 ml. of liquid ammonia was not discharged by 73 g. of hexamethyldisilazine, even after vigorous stirring.

Treatment with Trimethylchlorosilane.—No reaction was apparent upon the addition of 0.1 mole of trimethylchlorosilane to 0.2 mole of hexamethyldisilazine. The chlorosilane was subsequently reclaimed from the mixture by distillation (b. p. 57.3°).

Reaction with Hydrogen Chloride.—A 1-liter flask, equipped with a sealed stirrer, a reflux condenser and an inlet tube for hydrogen chloride, was charged with 600 ml. of dry benzene and 40.3 g. (0.25 mole) of hexamethyldisilazine. Stirring was begun and a stream of dry hydrogen chloride passed into the solution. A white solid immediately precipitated and continued to form as the addition progressed. After an excess of hydrogen chloride had been added the mixture was crudely distilled, about 100 ml. of distillate being collected. The solid remaining was filtered by suction and dried at 15–60 mm. giving 12.9 g. (96%) of ammonium chloride. The distillate was fractionally distilled giving 34.0 g. of trimethylchlorosilane, b. p. 53–63°, 31.1–31.4% Cl (the pure material has b. p. 57.7°, 32.6% Cl); this represents a 63% conversion to the chlorosilane. Titration of the benzene residue indicated the presence of an additional 2.1 g. of hydrolyzable chlorine.

Reactions of Trimethyl-N-methylaminosilane

Treatment with Sodium.—No apparent reaction occurred upon refluxing trimethyl-N-methylaminosilane, b. p. 71°, with sodium.

Treatment with Trimethylchlorosilane: Preparation of Heptamethyldisilazine.—An immediate reaction occurred between 30.9 g. (0.30 mole) of trimethyl-N-methylaminosilane and 10.9 g. (0.10 mole) of trimethylchlorosilane. The reaction mixture was refluxed overnight, cooled and filtered. Distillation of the filtrate gave 21.4 g. (61%) of heptamethyldisilazine, b. p. 143–147°.

Anal. Calcd. for $C_7H_{21}Si_2N$: neut. equiv., 175.3. Found: neut. equiv., 178.1, 177.5.

Triethylsilyl Derivatives

Ammonolysis of Triethylchlorosilane.—To one liter of liquid ammonia in a 2-liter Dewar flask was added 93 g. (0.62 mole) of triethylchlorosilane[6] over a four-minute period with efficient mechanical stirring. The reaction was vigorous, volatilizing much ammonia. Stirring was stopped shortly after the addition was complete, whereupon the insoluble ammonolysis products (*ca.* 50 ml.) settled as a lower liquid phase. The ammonia was allowed to boil off through a soda lime drying tube; a latter portion of the vapor so distilled was found, upon absorption in water, to give the camphor-like odor of triethylsilanol. After the temperature of the reaction mass had risen to 0°, 500 ml. of dry heptane was added and the mixture slowly warmed.

After standing overnight the contents of the Dewar were filtered and the heptane distilled from the filtrate. Fractional distillation gave 21.4 g. (26%) of triethylaminosilane, b. p. 136.8–137.8° (753 mm.), n^{20}D 1.4259–1.4260. Titration of this substance with 0.1 *N* hydrochloric acid in ether–water mixtures to the methyl orange endpoint gave erratic and high neutral equivalents, ranging from 141 to 148. Titration of a redistilled sample, b. p. 135.7° (748 mm.), n^{20}D 1.4259, without ether gave consistent but still somewhat high results.

Anal. Calcd. for $C_6H_{17}SiN$: neut. equiv., 131.3. Found: neut. equiv., 134, 134, 134.

The higher boiling ammonolysis products were distilled in a modified Claisen flask at 16 mm. After the collection of a small amount (5 ml.) of material at 45° seven fractions totalling 27.6 g., b. p. 110–130°, n^{20}D 1.433–1.450, were collected. The latter fractions probably consisted of a mixture of hexaethyldisiloxane and hexaethyldisilazine.[7]

The entire liquid ammonolysis products were taken up in ether and titrated with 5% hydrochloric acid to the methyl orange endpoint. The ether was distilled from the oily layer and the hydrolyzate then steam distilled. Distillation at atmospheric pressure of the readily volatile portion (39.6 g.) from the steam distillation gave 15.0 g. of triethylsilanol, b. p. 153.6–154.4° (758 mm.), n^{20}D 1.4320–1.4318. The remaining portions of the steam distillate were found to contain a great deal of amino nitrogen; complete hydrolysis was however effected by refluxing for one hour with a mixture of hydrochloric and acetic acids.

Summary

1. The following new organosilicon compounds have been prepared and identified: trimethyl-N-methylaminosilane, trimethyl-N-ethylaminosilane, trimethyl-N,N-diethylaminosilane, heptamethyldisilazine and triethylaminosilane.

2. From trimethylchlorosilane the only ammonolysis product was hexamethyldisilazine. However, the stable primary amine $(C_2H_5)_3SiNH_2$ was produced from triethylchlorosilane.

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[6] This sample, b. p. 146.5–146.8°, was provided by C. P. Haber of this Laboratory who prepared it from ethylmagnesium chloride and silicon tetrachloride.

[7] Kraus and Nelson's statement (ref. 5) that this amine "distills at 100° under a pressure of 1 mm." probably does not refer to the true boiling point of the substance.

SCHENECTADY, NEW YORK RECEIVED AUGUST 9, 1945

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Further Investigations of Polarity in Hydrocarbons Possessing Conjugated Systems

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

Hyperconjugation in butadiene, and in 1-methyl-, 2-methyl-, and 2,3-dimethylbutadiene has been investigated by means of dipole moment measurements.[1] The investigations were continued more than two years ago on other related molecules, but, because of lack of time resulting from war conditions, the results have not hitherto been written up for publication.

The dielectric constants of the vapors were measured with the apparatus and technique previously described.[2] The measurements on cyclopentadiene 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 deviations from the gas laws were eliminated by several measurements over a wide range of pressure.

Materials

1,2-Dimethylbutadiene-1,3,1,3-Dimethylbutadiene-1,3,-2-Ethylbutadiene-1,3.—Materials kindly furnished by the Carbide and Carbon Chemicals Corporation were believed to be of high purity. They contained no inhibitor as they polymerize relatively slowly. Any polymer that might possibly have formed would have been removed by the double distillation carried out in the vacuum system before the vapors were admitted to the measuring cell.

Cyclopentadiene.—Dicyclopentadiene from the United States Steel Corporation was kindly furnished by the du

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[1] Hannay and Smyth, THIS JOURNAL, **65**, 1931 (1943).

[2] McAlpine and Smyth, *ibid.*, **55**, 453 (1933); de Bruyne and Smyth, *ibid.*, **57**, 1203 (1935); Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).