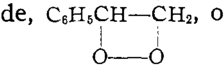
$$dP/dt = K - K'P$$

that is, the simultaneous formation (from some steady-state process) and decomposition of peroxide.

It would seem that the initiation process could be represented by activated styrene reacting with oxygen to yield a peroxide readical which disproportionates to benzaldehyde and formaldehyde.[20] The energy-rich benzaldehyde, possibly together with the formaldehyde may carry on the chain reaction as suggested by Medvedev and Zeitlin.[5] The short chain length found in this work is explicable on the basis of a chain carrier with a short mean free life, which would be expected for an energy-rich molecule. It is not clear whether the peroxide that accumulates slowly is the resonance stabilized peroxide, $C_6H_5CH—CH_2$, or a further reaction product.



$$\underset{|\quad\quad\;|}{C_6H_5CH—CH_2} \atop {O—O}$$

Our conclusions are necessarily dependent upon the assumption that the antioxidants almost completely suppress the chain reaction. This would seem to be difficult to prove experimentally but seems likely, inasmuch as such antioxidants prevent the formation of catalysts (peroxides produced by the action of oxygen on the monomer and accumulated benzaldehyde) capable of initiating polymerization, and that this inhibition operates as long as excess antioxidant is present. On the other hand it must be admitted that the inactivation of all peroxide radicals with the antioxidants employed is not infrequently found to be a difficult thing to do.

Bolland and Ten Have[21] have studied the relative efficiencies of the inhibitory effect of phenolic compounds on the thermal oxidation of ethyl linoleate. These compounds differ in their efficiency (as measured by oxygen consumption in the presence and absence of antioxidant) according to their oxidation–reduction potential and concentration. Thus, catechol is only about 0.6 times as efficient as hydroquinone. As is evident from Fig. 7 of this work *t*-butylcatechol is as efficient as hydroquinone in suppressing oxygen consumption (the styrene was saturated with antioxidant in both cases). This equality in efficiency is explicable on the basis that nearly all the oxidation chains are stopped.

The results on peroxide formation and benzaldehyde formation support the usual concepts of an autoxidation process with a peroxide occurring as an intermediate compound in the process.

It is a pleasure to acknowledge the support of the United States Rubber Company in connection with this work.

Summary

A magnetic susceptibility method has been used to measure the rate of oxygen consumption during the initial stages of styrene polymerization. Measurements were made with and without the addition of antioxidants. The rates of formation of peroxide and of benzaldehyde in this system have also been determined.

From these data calculations were made of the rate constant for initiation and the kinetic chain length for the reaction of oxygen with styrene, as well as the activation energy for initiation.

EVANSTON, ILLINOIS RECEIVED JUNE 9, 1949

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(21) J. L. Bolland and P. Ten Have, *Discussions of the Faraday Soc.*, **252** (1947).

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORIES, TULANE UNIVERSITY]

The Dipole Moments of Some Derivatives of Trichlorosilane

BY H. O. SPAUSCHUS, A. P. MILLS,[1] J. M. SCOTT AND C. A. MACKENZIE

The dipole moments have been determined for a series of ethyl and ethoxy derivatives of trichlorosilane. The compounds investigated were trichlorosilane, ethyldichlorosilane, diethylchlorosilane and triethoxysilane; all measurements were made in benzene solution.

Previous investigators have measured the dipole moments of tetraethoxysilane,[2] some chlorosilanes,[3] silicobromoform,[4] ethyl and phenyl derivatives of tetrachlorosilane and tetrafluorosilane,[5] and compounds containing triethylsilyl and triphenylsilyl radicals.[6]

Experimental

Dielectric Constant.—All measurements were made using a heterodyne beat apparatus similar to that of Hudson and Hobbs[7] with several modifications to increase the stability. The experimental cell and precision condenser (General Radio Company, type 722-D) were kept in a constant temperature air bath at 25.00 ± 0.05°. The variable oscillator was also kept at a constant temperature to minimize possible frequency drift. Radio broadcasts were used as sources of constant frequency. All capacity measurements were made at three different frequencies. The all glass experimental cell consisted of two concentric cylinders coated with platinum, and had a volume of

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(1) Present address: Dept. of Chemistry, University of Miami, Miami, Florida.

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(3) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

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(6) L. Malatesta and R. Pizzotti, *Gazz. chim. ital.*, **72**, 491 (1942); **73**, 143 (1943).

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about 25 ml. The electrical capacity of the cell was approximately 55 micromicrofarads.

Density.—The densities of the silane–benzene solutions were determined at 25° with a 15-ml. specific gravity bottle. Since the trichloro-, diethylchloro-, ethyldichloro- and triethoxysilanes are readily hydrolyzed on contact with moist air, special precautions were observed in preparing the silane–benzene solutions. The silanes were distilled directly into weighed bulblets which were sealed off, reweighed, and then crushed beneath the surface of the benzene. Hydrolysis was thus kept at a minimum since solutions prepared in this manner showed very little or no cloudiness.

Molar Refractions.—The molar refractions were calculated from densities and refractive indices measured in this laboratory.[8] In all cases these molar refractions check quite closely with those predicted using the method of Sauer.[9]

Materials.—J. T. Baker C. P. benzene was frozen and the first fraction to melt was discarded. The remainder was then distilled from phosphorus pentoxide. The boiling point of the fraction used in these measurements was 79.9–80.0° at 761 mm. and its refractive index was $n^{25}D$ 1.4980.

The silanes were prepared in this Laboratory and purified by fractionation using a column packed with glass helices and having about 15 theoretical plates. The boiling point ranges, corrected to 760 mm., of the samples measured are listed in Table I.

TABLE I

Compound	Boiling point range, °C.	Molar refraction Exptl.	Predicted
Trichlorosilane	31.6– 32.0	24.57	24.76
Ethyldichlorosilane	74.7– 75.0	29.53	29.61
Diethylchlorosilane	99.6– 99.9	34.61	34.52
Triethylsilane	107.5–107.9	39.49	39.49
Triethoxysilane	131.2–131.8	42.15	42.18

Experimental Results.—The mole fractions (N_2) of silane, the densities ($d_{1,2}$) and dielectric constants ($E_{1,2}$) of the silane–benzene solutions and the calculated polarization values (P_2) for the solute are listed in Table II. Graphing of the $E_{1,2}$–N_2 data indicated a linear relationship in all cases. The constants for the first degree equations were obtained by the method of least squares and the intercepts are the tabulated values for the dielectric constants of the pure solvent, benzene. This procedure has been suggested previously and its advantages discussed in the literature.[10,11] The P_{2_0} values, representing the polarization of the solute at infinite dilution, were obtained by extrapolation of P_2–N_2 plots. The atomic polarization was taken to be equal to 5% of the electronic polarization contribution.

TABLE II

N_2	$d_{1,2}$	$E_{1,2}$	P_2
	Trichlorosilane		
0.00000	0.87326	2.2716	P_{2_0} = 45.00
.00206	.87402	2.2739	51.38[a]
.00303	.87469	2.2743	44.78
.00943	.87788	2.2785	42.00
.01580	.88146	2.2860	43.72
	Ethyldichlorosilane		
0.00000	0.87326	2.2691	P_{2_0} = 116.2
.00477	.87427	2.2940	113.8
.00923	.87542	2.3185	114.9
.01576	.87737	2.3520	112.3
.02170	.87876	2.3839	112.6
	Diethylchlorosilane		
0.00000	0.87298	2.2713	P_{2_0} = 119.5
.00159	.87300	2.2796	118.5
.00314	.87302	2.2876	117.7
.00719	.87305	2.3084	117.2
.01224	.87309	2.3347	117.2
	Triethylsilane		
0.00000	0.87271	2.2699	P_{2_0} = 52.8
.00564	.87094	2.2719	54.46
.00919	.86991	2.2716	51.76
.01408	.86858	2.2725	51.41
.02048	.86672	2.2739	51.62
.02857	.86455	2.2762	51.82
	Triethoxysilane		
0.00000	0.87271	2.2730	P_{2_0} = 108.9
.00556	.87260	2.2902	102.2
.00567	.87257	2.2915	104.6
.00804	.87278	2.3010	107.1
.01772	.87295	2.3327	105.5
.02630	.87332	2.3600	104.4

[a] This solution showed considerable hydrolysis.

Discussion

The results of the dipole moment determinations are given in Table III.

TABLE III

Compound	$\mu \times 10^{18}$
Trichlorosilane	0.97 ± 0.06
Ethyldichlorosilane	2.04 ± 0.04
Diethylchlorosilane	2.01 ± 0.02
Triethylsilane	0.75 ± 0.07
Triethoxysilane	1.78 ± 0.06

The value of 0.97D for trichlorosilane is considerably higher than 0.85D reported by Brockway and Coop[3] for the same compound using the temperature variation method. A similar situation may be noted in the moments reported for chloroform by different investigators.[12] The solution method yields values averaging 0.13D higher than those obtained from measurements on the vapor.

Moments for ethyldichlorosilane and diethylchlorosilane have not been reported in the literature. Comparison of the dipole moment of 2.04D for ethyldichlorosilane with the moment of 2.06D reported for 1,1-dichloropropane[13] shows the silicon compound to have a slightly lower electric moment than the analogous carbon compound. A similar condition was noted by Brockway and Coop[3] in their comparison of moments of chlorin-

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ated methanes and silanes. It is difficult to give a satisfactory explanation for this trend since considerations of electronegativity differences, bond distances, and the effect of the size of the central atom all lead to predictions of a larger moment for the silicon compounds.

The moment for triethylsilane was reported[6] as being small but positive. A consideration of the factors contributing to the moment in this molecule indicates that the value $0.75D$ is plausible. If it is assumed that the Si–C and Si–H bonds are directed tetrahedrally, then the contribution to the moment of the molecule due to electronegativity differences is readily calculated. Using the electronegativity differences of $0.7D$ for the Si–C bond and $0.3D$ for the Si–H bond,[14] the resultant moment is $0.4D$. This rough calculation neglects increases in the moment caused by polarization of the ethyl groups and rotational contributions. Such contributions provide an explanation for the dipole moment found.

An exact calculation of a dipole moment for triethoxysilane is difficult since the rotational contribution of the three ethoxy groups must be taken into consideration. Assuming an Si–O electronegativity difference of $1.7D$,[14] the vertical component of the three Si–O bonds is $1.7D$. This is opposed by the $0.3D$ contribution of the Si–H bond, giving a resultant of $1.4D$. A value of $0.38D$ for the rotational and vibrational contributions would be required to produce agreement between the experimental and theoretical results. The rotational contribution of the ethoxy groups, assuming free rotation, sometimes aids the moment due to the Si–O and Si–H bonds and sometimes opposes it. This can be shown by calculating the dipole moments of two possible symmetrical structures. In one structure the moments of three C–O bonds are acting parallel to and opposing the resultant moment of the Si–O and Si–H bonds. If we assign the C–O bond a value of $1.1D$, the moment due to the three C–O bonds will be $-3.3D$, and the structure will have a resultant moment of $-1.9D$. In the other structure, the three C–O bonds are acting at an angle of 40° with the resultant moment of the Si–O and Si–H bonds and aiding it. The moment due to the three C–O bonds will be $+2.5D$, and the structure will have a resultant moment of $+3.9D$. If both of the structures are assumed to be sterically possible, the dipole moment can vary from $+3.9D$ to 0 to $-1.9D$. The experimental value of $1.78D$ is near the mean value of $1.64D$ calculated by assuming all values within the range to be equally probable.

Summary

1. The dipole moments of trichlorosilane, ethyldichlorosilane, diethylchlorosilane, triethylsilane and triethoxysilane were determined in benzene solution and were found to be 0.97, 2.04, 2.01, 0.75 and $1.78D$, respectively.

2. The measured moments are discussed in relation to the structure of the molecules.

NEW ORLEANS, LOUISIANA RECEIVED JULY 5, 1949

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[14] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 64.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Oxidation Potentials and Ultraviolet Absorption Spectra of a Series of Normal Ketones

BY R. A. DAY, JR., A. E. ROBINSON, JR., J. M. BELLIS AND S. B. TILL

Owen, Quayle and Clegg[1] of this Laboratory reported the surface tensions and parachors of a series of fifteen normal chained ketones of eleven or less carbon atoms. They evaluated the constitutive variations in the parachor value of the carbonyl group as different alkyl groups are attached. It was considered of interest to measure some other properties of this same series of ketones to determine whether or not variations similar to those observed in the parachor would occur. The present paper is a report of the measurements of oxidation potentials and near ultraviolet absorption spectra of this series of ketones.

Experimental

Oxidation Potentials.—The ketones were equilibrated against fluorenone in the presence of aluminum *t*-butoxide by the method previously described for many ketones.[2] Equilibrium concentrations of fluorenone were measured, however, by the colorimetric procedure described below rather than polarographically.

Ultraviolet Absorption Spectra.—These measurements were made with a Beckman model DU spectrophotometer. All solutions were $0.04\ M$ ketone in methanol. Measurements were made from 220 to 320 mμ at 5-mμ intervals. In the vicinity of maximum absorption readings were taken at 2-mμ intervals.

Purity of Materials.—All distillable reagents were carefully fractionated through a 9-plate column packed with glass helices. The samples taken for measurement were from the center of the fractions of constant refractive index.

Fluorenone (Eastman Kodak Co.) was recrystallized according to Baker and Adkins,[2] m. p. 82–83°; fluorenol, prepared as described,[2] melted at 154–155°. A saturated solution of aluminum *t*-butoxide used ("Organic Syntheses"[3]) in dry toluene was found to be $0.70\ M$ in alkoxide.

At one time during the course of the work, considerable trouble was encountered from a side reaction between fluorenol and aluminum *t*-butoxide. Fluorenone is a prod-

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(3) "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 8.