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 0.75*D* 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 0.7*D* for the Si–C bond and 0.3*D* for the Si–H bond,[14] the resultant moment is 0.4*D*. 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 1.7*D*,[14] the vertical component of the three Si–O bonds is 1.7*D*. This is opposed by the 0.3*D* contribution of the Si–H bond, giving a resultant of 1.4*D*. A value of 0.38*D* 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 1.1*D*, the moment due to the three C–O bonds will be −3.3*D*, and the structure will have a resultant moment of −1.9*D*. 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 +2.5*D*, and the structure will have a resultant moment of +3.9*D*. If both of the structures are assumed to be sterically possible, the dipole moment can vary from +3.9*D* to 0 to −1.9*D*. The experimental value of 1.78*D* is near the mean value of 1.64*D* 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 1.78*D*, respectively.

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

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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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[1] Owen, Quayle and Clegg, THIS JOURNAL, **64**, 1294 (1942).

[2] Baker and Adkins, *ibid.*, **62**, 3305 (1940).

[3] "Organic Synthesis," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 8.

uct of this reaction. Cox and Adkins[4] noted such a reaction for a number of carbinols, although it normally produced only a small amount of ketone. It is believed that an impurity in the catalyst, or perhaps slight hydrolysis of the catalyst, accelerates the reaction with fluorenol. A carefully repurified sample of the alkoxide produced only about the same degree of reaction with fluorenol as that observed by Cox and Adkins with other carbinols.

Method of Analysis.—A spectral-transmission curve of fluorenone in toluene showed that the ketone absorbs light strongly around 410 mμ. A plot of log transmittancy at this wave legnth *vs.* concentration of ketone gave a straight line at concentrations of about 4 to 10% fluorenone.[5] Fluorenone could be determined satisfactorily from the optical density of a suitably diluted reaction mixture.

Reaction mixtures were prepared from the following toluene solutions: (A) 0.05 *M* in fluorenol and the ketone being studied, (B) 0.05 *M* in fluorenone and the carbinol of the ketone in A, and (C) a saturated solution of aluminum *t*-butoxide. Duplicate reaction solutions of two percentages, one higher and one lower than the expected equilibrium percentage, were prepared. The volume of A + B totaled 10 ml., to which 1 ml. of C was added. The two complements of nitrogen-filled, sealed ampoules were then heated in an electric oven at 60° for different time intervals.

The unknown cell solutions were made by diluting 2 ml. of the reaction solution with 10 ml. of toluene. Transmittancies of duplicate samples were compared to ensure that equilibrium had been reached. (It was not found necessary to hydrolyze the aluminum *t*-butoxide.) Three standard cell solutions were prepared from solution D (10 ml. of B diluted with 55.5 ml. of toluene) so as to be of lower concentration than the expected equilibrium concentration. Either unknown and the three standards were transferred each to one of four cuvettes and colorimetric comparison was made at 410 mμ to obtain the percentage transmittancy of the unknown referred to 100% transmittancy by each standard. Extrapolation of the straight line resulting from a plot of transmittancy *vs.* concentration to a value of 100% transmittancy gave the concentration of the unknown. All volumetric apparatus was calibrated.

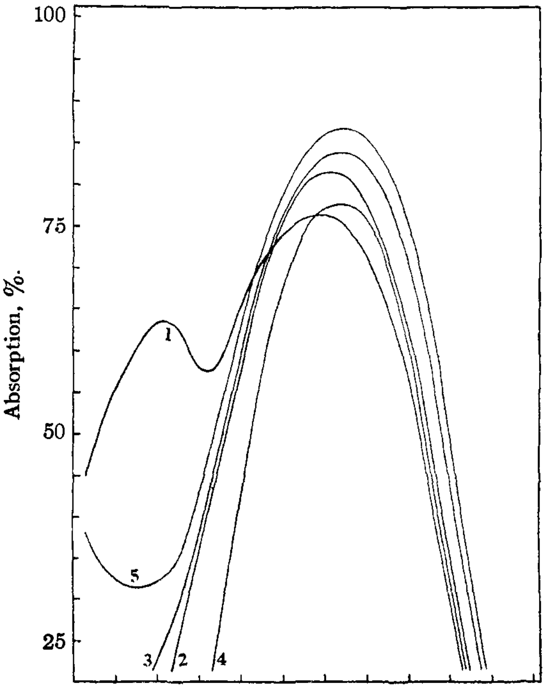

Fig. 1.—(1), MM; (2), ME; (3), MP; (4), MB; (5), MA.

The accuracy of the method was tested by running seven determinations in which the entire procedure was followed except that toluene was substituted for the solution of the catalyst. The average deviation of the determined concentrations from the known was 0.2%. The largest deviation was 0.3%. A run was also analyzed both polarographically and colorimetrically. The results agreed to within 0.5%.

Results

The results of the measurements are summarized in Table I. All potentials were calculated from the normal potential of fluorenone of 117 mv.[6] The free energies of reduction, calculated from the equation $-\Delta F = nFE_0$, are also listed in Table I. It will be noted that there is a general decrease in the normal potential as the size of the alkyl groups is increased. The decrease in any one series as only one of the carbon chains attached to the carbonyl is lengthened is appreciable, however, only in the methyl series.

Table I

Oxidation Potentials and Ultraviolet Absorption Data

Ketone	Eq. % fluorenone	E_0, mv.	$-\Delta F$, kcal.	$\lambda_{max.}$, mμ.	Molar abs. index
MM	61.3	129	6.0	269	14.9
ME	55.8	123	5.7	272	18.2
MP	54.4	122	5.6	274	19.7
MB	54.8	122	5.6	275	16.4
MA	54.1	121	5.6	274	21.7
EE	50.6	118	5.4	273	20.2
EP	49.6	117	5.4	276	22.8
EB	49.0	116	5.3	275	24.8
EA	49.6	117	5.4	278	23.7
PP	42.8	110	5.1	278	24.8
PB	42.6	109	5.0	278	26.3
PA	42.1	109	5.0	279	26.1
BB	35.0	101	4.7	278	28.5
BA	36.6	103	4.7	279	28.0
AA	29.8	95	4.4	278	49.0

All of the ketones show the characteristic carbonyl absorption in the range of 269 to 279 mμ. The spectral-absorption curves are shown in Figs. 1, 2 and 3. The wave length of maximum absorption and the molar absorbency index at this wave length are listed in Table I. Both hyperchromic and bathochromic effects are evident as the size of the alkyl groups attached to the carbonyl increases.

The results of both series of measurements are in accord qualitatively with the concept that larger normal aliphatic groups show a greater electron release than smaller groups. Such an effect should increase the ease of polarization of the car-

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[4] Cox and Adkins, This Journal, **61**, 3364 (1939).

[5] The percentage system is herein employed to signify that mole per cent. of total ketones which is fluorenone, as in Baker and Adkins.[2]

[6] Homer Adkins, private communication.

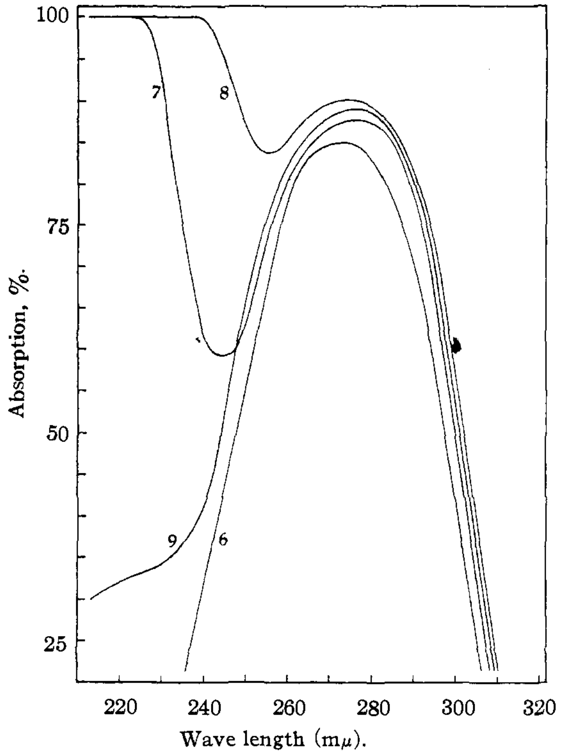

Fig. 2.—(6), EE; (7), EP; (8), EB; (9), EA.

bonyl linkage, increasing the ease of absorption of light. In a chemical reaction the attack on the carbonyl would occur at the positively charged carbon atom. Thus the oxidation potential should decrease with increasing ease of electron release of the attached group. The observed decrease in the carbonyl contribution to the parachor[1] is also in accord since an increase in ease of polarization of the carbonyl (total polarization giving in effect a semi-polar bond) would lead to a decrease in molecular volume as measured by the parachor.

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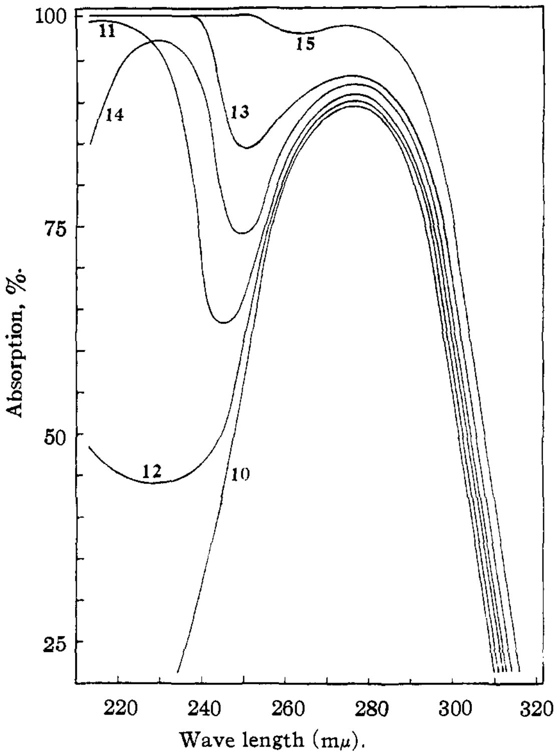

Fig. 3.—(10), PP; (11), PB; (12), PA; (13), BB; (14), BA; (15), AA.

Summary

The oxidation potentials of a series of fifteen normal chained ketones of eleven or less carbon atoms have been measured.

The near ultraviolet spectra of the ketones in methanol solution have also been investigated.

A decrease in oxidation potential and both bathochromic and hyperchromic effects in the absorption spectra are observed as the size of the alkyl groups attached to the carbonyl is increased. These results are in qualitative accord with the previously observed decrease in the carbonyl contribution to the parachor as the size of the alkyl groups is increased.

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