[Contribution from the Chemical Laboratory of Harvard University]

Single Bond Energies. IV. The Vapor Pressure of Hexaphenylethane

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The first three papers of this series[1] present data on the heat of oxidation and hydrogenation of certain organic free radicals. From these data conclusions are drawn regarding the strength of the C–C bond in the substituted ethane which gives rise to a free radical on dissociating.[2] If one makes certain assumptions regarding the strength of single bonds, one can calculate the effect of steric hindrance in the substituted ethane, which shows up as an increased heat of oxidation or hydrogenation. Without making any assumptions regarding the absolute values for single bond energies, one can compare various substituted ethanes and determine the relative significance of steric hindrance in passing from one to another. Finally one can estimate the significance of resonance energy in each case in promoting dissociation.

The above study led to the conclusion that both steric hindrance and resonance are very important factors in describing the behavior of free radicals. Furthermore these two factors may vary in passing from one free radical to another in such a way as largely to cancel each other and therefore give no evidence of their importance in a determination of the degree of dissociation alone.

The results heretofore reported have been obtained by a study of reactions involving solutions only. In order to draw conclusions free from uncertainty introduced by the presence of solvent, we determined to carry out experiments which would enable us to calculate the heat of oxidation and hydrogenation in the vapor state. Presumably these experiments would also give an answer to the time-honored question of the importance of the solvent in the whole phenomenon of the existence of free radicals. The experiments of Ziegler and Ewald[3] make it seem very probable that the solvent is not of prime importance since the free energy and the heat of dissociation are not greatly affected by a change in solvent. Nevertheless, a direct determination of the importance of the solvent is greatly to be desired.

The problem of determining the vapor pressure of a free radical is not easy. The instability of the compound precludes the possibility of working at elevated temperatures and the extremely low vapor pressure of even the simplest free radical at ordinary temperatures eliminates most methods of study. We have chosen a quartz fiber gage. Coolidge has greatly improved the design of this gage and has suggested its use in such problems as the one in hand.[4] From the vapor pressure curve can be calculated the heat of sublimation of hexaphenylethane. Similar measurements on triphenylmethane and on the peroxide formed in the oxidation of hexaphenylethane then give data which can be combined with the values obtained for the heat of hydrogenation and oxidation of hexaphenylethane in solution. We have already reported data on the heats of solution and therefore have a method for calculating the heat of hydrogenation and of oxidation in the vapor phase. From these data we may discover the effect of the solvent on the heat of the reaction and can estimate the effect on the free energy of dissociation.

As Coolidge has pointed out, it is not possible to determine with the quartz fiber gage the molecular weight of a vapor, some independent means of measuring the pressure being necessary for this purpose. It seemed barely possible, however, that a temperature and concentration might be available at which dissociation of the ethane was incomplete and the temperature dependence of the pressure would then give the second desired relation necessary for a determination of the molecular weight. This did not prove to be the case and we were therefore forced to devise additional experiments in order to solve this part of the problem. The most convenient determination seemed to be that of the vapor density. Unfortunately this part of the work is incomplete at the present time. Since the work has been temporarily interrupted it seems best to report progress to date.

Materials

The hexaphenylethane was part of the material used in the work reported in the first two papers of this series. The determination of the purity of the material by means

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(1) Bent, *et al.*, This Journal, **58,** 165, 170, 1624 (1936).

(2) See also, *ibid.*, **57,** 1245 (1935); Pauling and Wheland *J. Chem. Phys.*, **1,** 362 (1933).

(3) Ziegler and Ewald, *Ann.*, **473,** 163 (1929).

(4) Coolidge, This Journal, **45,** 1637 (1923).

of oxygen absorption indicated that any impurity was probably not more than 1%. The sample of triphenylmethyl peroxide was also prepared in connection with the oxidation of hexaphenylethane and was purified by recrystallization. The sample of triphenylmethane, after crystallization, melted at 92.1 ± 0.1°.

Experimental Procedure

The quartz fiber gage is of the type described and developed by Coolidge.[4] In order to simplify the calculations the fibers were made rather long (about 15 cm.) and small in diameter. The loss of energy in the fiber thus becomes so small as to be entirely negligible. When the gage is highly evacuated, many hours are required for the amplitude to die down to one-half while in the course of ordinary measurements the time required is from twenty to one hundred seconds. This justifies the neglect of the energy dissipated in the fiber.

The gage was calibrated by measuring the pressure of nitrogen with the quartz fiber gage and a McLeod gage. As a second method it was calibrated by measuring the pressure of mercury at various temperatures. The latter method agrees quite well with the former and has been used to calculate the constant "b" in the equation

$$\log p = \log \ln A_1/A_2 - \log b + {}^1/_2 \log T - {}^1/_2 \log M - \log t$$

in which p is the pressure expressed in millimeters of mercury, A_1 and A_2 are the amplitudes of the fiber, usually being about 10 and 5 mm., respectively. b is a constant characteristic of the fiber, M is the molecular weight, T is the absolute temperature and t is the time required for the fiber to die down from A_1 to A_2. The following table will indicate the reliability of the gage, the value of log b being 0.665. The values for the vapor pressure of mercury are calculated by the formula[5]

$$\log p = 8.99393 - 3250/T - 0.30 \log T - 0.00018\, T$$

in which p is expressed in millimeters.

TABLE I

THE VAPOR PRESSURE OF MERCURY

Temp., °C.	Pressure, mm. Found	Pressure, mm. Calcd.
16.8	0.00097	0.00099
29.8	.00291	.00294
40.8	.00781	.00789
49.0	.0127	.0124
52.2	.0158	.0156
52.4	.0160	.0158

At the beginning of a run the gage and tube in which the sample is to be placed are baked at 400° for several hours while evacuating the apparatus to a pressure of 10^{-5} mm. The apparatus is then allowed to cool and the capsule containing the triphenylmethane broken and allowed to drop down into the apparatus. The tube containing the capsule and magnetic hammer is sealed off and the triphenylmethane twice sublimed to different parts of the tube with intermittent pumping to remove gases which might be liberated. In making a measurement the system is pumped, using a liquid air trap, to remove any foreign gas and then the system shut off from the pump and trap by means of a magnetically controlled ground-glass stopper. The fiber is set oscillating by means of a slight impulse given to the furnace in time with the natural frequency of the fiber. A micrometer eyepiece on a telescope serves to give any convenient change in amplitude, the time required for this change being noted with a stop watch. After taking a reading the system is again pumped at the same temperature and the pressure again determined.

The thermostat is an electrically heated air-bath with windows of thin mica and a blower within the thermostat to circulate the air. The reasons for choosing an air thermostat (which of course cannot be regulated easily with high precision) are to allow high temperatures for baking the apparatus, to avoid parallax in reading the gage, and to be able to change the temperature rapidly in the case of hexaphenylethane in order to avoid decomposition as much as possible.

In the case of hexaphenylethane and the peroxide it was not possible to sublime the material without undue decomposition. Probably some of the earlier determinations are in error on account of foreign gas. However, the final runs which are here reported indicate that the method of pumping just before each determination gave reproducible results which could be repeated with either a rising or falling temperature.

As was to be expected, decomposition took place with both the ethane and the peroxide. We therefore made careful measurements of the pressure over a period of time sufficiently long to enable us to extrapolate back to zero time for the true pressure. Fortunately the rate of decomposition is less than the rate of evaporation or this procedure would not have been possible. The pressure turns out to vary nearly as a linear function of the time so that it is possible to take the time required for the fiber to decrease in amplitude by a given amount as an accurate measure of the pressure at the mid-point of this time interval. This may readily be justified as follows. If we assume that the pressure is a linear function of the time and is represented by the expression

$$p = \alpha + \beta t$$

we can substitute this in the expression given for the gage[4] to give

$$\mathrm{d}A/A\mathrm{d}t = a + b\sqrt{M}\,(\alpha + \beta t)$$

Neglecting the constant "a" which we have shown to be justified for this gage we have on integration

$$1/t \ln A/A_0 = b\sqrt{M}\,(\alpha + \beta t/2)$$

which enables one to solve for the quantity in parentheses, namely, the pressure at a time half-way between the initial and the final time for the gage reading. These values for the pressure, when plotted against the total time, since the apparatus was closed from the pump, give a smooth curve which can be extrapolated back to zero time to give the pressure which would be obtained if no decomposition had taken place. The error introduced by this extrapolation is probably of the order of 10% in the pressure.

Discussion of Experimental Results

The experimental values for the pressure are given with the values calculated from the following equations. For triphenylmethane the pres-

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(5) C. A., 28, 4935 (1934).

sures can be expressed by the equation $\log p = -5260/T + 12.72$, which gives a value for ΔH of 24.1 ± 1.0 kcal. For hexaphenylethane the equation is $\log p = -5987/T + 12.85$, giving a value for ΔH of sublimation of 27.4 ± 1.5 kcal. For triphenylmethyl peroxide the equation is $\log p = -8259/T + 16.98$ and the value for ΔH is 37.8 ± 1.5 kcal.

TABLE II

VAPOR PRESSURE OF TRIPHENYLMETHANE, HEXAPHENYL ETHANE AND TRIPHENYLMETHYL PEROXIDE

Temp., °C.	Pressure, mm.	
	Found	Calcd. by eq.
	Triphenylmethane	
26.5	0.000026[a]	0.0000148
46.0	.000181	.000174
46.5	.000199	.000186
46.6	.000201	.000188
59.35	.000773	.000796
60.8	.000980	.000937
75.2	.00444	.000420
75.6	.00459	.00436
87.6	.0123	.0139
90.5	.0146	.0181
	Hexaphenylethane, Run 1	
75.4	0.0000541	0.0000479
76.5	.0000633	.0000537
90.6	.000253	.000246
106.0	.001053	.001150
106.2	.001038	.001180
120.8	.00419	.00447
	Run 2	
92.7	.000283	.000309
93.6	.000306	.000339
105.8	.000997	.00112
106.0	.000935	.00115
76.8	.0000464	.0000550
121.8	.00512	.00490
	Triphenylmethyl peroxide	
119.8	0.000125	0.000091
129.3	.00038	.00029
129.8	.00029	.00031
140.3	.00122	.00102
140.4	.00077	.00102
151.4	.0044	.0034
161.0	.0089	.0091

[a] The experimental values at low pressures may be brought into agreement with those calculated from the equation by assuming the presence of foreign gas to the extent of about 10^{-5} mm.

We may now combine these values with those previously reported for the heat of oxidation and hydrogenation of solid hexaphenylethane to give solid product. We thus obtain a value for the heat of hydrogenation of gaseous hexaphenylethane of −19.7 kcal. and of oxidation of gaseous hexaphenylethane of −35.1 kcal. We may compare these values with the values to be predicted from single bond energies and thermal data of −8 and −4 kcal. The fact that the energy change for the reaction in the gaseous phase is so much more negative than that predicted, we take to be an indication of the steric hindrance in the molecule. The weakening of the C–C bond is therefore inferred to be equivalent to 12 kcal. if we consider the reaction of hydrogenation and 31 kcal. if we consider the oxidation. The agreement between these two figures is not satisfactory but at present we have no explanation.

The measurements on the rate of decomposition shed some light on the nature of this reaction. The reaction appears to be a unimolecular reaction with zero heat of activation, one of the products of the reaction being triphenylmethane. The rate of decomposition, as measured by the increase in pressure while the gage was open to the sample but closed from the pump, varied from $1\text{–}5 \times 10^{-3}$. However, as the concentration was varied by a factor of 200 and the temperature by 45° the variation in rate probably is not significant. Furthermore, the variation in rate was little more than the variation obtained in successive runs at a given temperature and when plotted gave no indication of a variation dependent upon the temperature. The product of the reaction was identified by a mixed melting point as triphenylmethane. Other products are also formed of high molecular weight and having a yellow color.

The rate of decomposition of the peroxide appeared to be much more reproducible and in fact a plot of the log of the rate constants against the reciprocal of the absolute temperature permits one to draw a smooth curve through the points. However, the curve has a maximum at about 140° and therefore we attach little significance to these data. The activation energy for the decomposition as determined from the lower part of the curve is roughly 30 kcal.

The data on the heat of vaporization of triphenylmethane and hexaphenylethane give a pretty conclusive answer to the question of dissociation in the vapor phase. The value for triphenylmethane is 24.1 and for hexaphenylethane is 27.4. We would expect the latter compound to have a greater heat of vaporization on account of its greater molecular weight. The most probable explanation of these figures is that hexaphenylethane is not dissociated in the vapor state and that the value 27.4 represents the true heat of vaporization of hexaphenylethane. The possibility of dissociation being negligible at the lower temperatures but becoming important at higher temperatures is ruled out on account of the straight line obtained by plotting log p against $1/T$. Dissociation would increase the pressure, the partial pressure of the undissociated material being that given by the sublimation pressure of the ethane at that temperature. Hence the curve would be convex toward the temperature axis. Almost complete dissociation of the ethane at all temperatures reported in this work would give a straight line plot but seems very improbable for two reasons. In the first place the total pressure would have to be the sublimation pressure of the ethane plus the pressure of the free radical. If the ethane were practically completely dissociated, this would lead to a total pressure of perhaps 100–1000 times that of the ethane, since the solid ethane would have to be in equilibrium with its vapor. This is not compatible with the observed pressure which is only 1/100 of that of triphenylmethane at about 90°. Furthermore, the slope of the curve would give in this case half the heat of dissociation plus half the heat of sublimation of the ethane. If we were to assume 10 kcal. for dissociation, this would lead to 50 kcal. for sublimation, which seems unreasonably large when compared with the value of 24.1 for triphenylmethane. The fact that hexaphenylethane has twice the molecular weight of triphenylmethane would not lead to doubling the heat of sublimation, as an increase of only 50% is observed in going from triphenylmethane to the peroxide.

If we assume that the dissociation is less than 10% at the lowest temperature, we can calculate that ΔF must be at least + 15 kcal., expressing concentrations in atmospheres. If there is an increase in entropy on dissociation, as seems very probable, the value for ΔH of dissociation in the vapor state may be considerably more than 15 kcal.

Summary

1. The vapor pressures of triphenylmethane, hexaphenylethane and triphenylmethyl peroxide have been measured by means of a quartz fiber gage.

2. The values calculated for the heat of vaporization of these compounds indicate that the C–C bond in hexaphenylethane in the vapor state is weaker than a normal C–C bond. The heat of dissociation, however, is probably greater than that found for hexaphenylethane in solution.

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[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Equilibria in the Saturated Solutions of Salts Occurring in Sea Water. II. The Quaternary System $MgCl_2$–$CaCl_2$–KCl–H_2O at 0°

BY IVER IGELSRUD WITH THOMAS G. THOMPSON

No data on the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O occur in the literature. This system is of importance in the study and utilization of the secondary salts in natural deposits originating from sea water. Data at lower temperatures are important to an adequate understanding of the geological processes to which the natural salts and their solutions are subject during cold winter periods.

A survey of the literature on the bounding ternary systems, together with data for their 0° isotherms, has been given in a previous paper.[1] The experimental procedure, the methods of purification of the salts, and the methods of chemical analysis used in the study of the quaternary isotherm were the same as for the ternary systems. Samples of the saturated solutions and solid phases in equilibrium were taken for chemical analysis as described. The time found sufficient for the attainment of equilibrium in the quaternary system was from twelve to fifteen hours as compared with eight to ten hours for the ternary solutions.

The results of the chemical analyses for solutions and residues are given in Table I. The data for the saturated solutions are depicted graphically in Figs. 1, 2 and 3. Figures 4 and 5 illustrate the methods used for the identification of the solid phases.

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[1] Iver Igelsrud and T. G. Thompson, THIS JOURNAL, **58**, 318 (1936).