TABLE II

SUMMARY OF DERIVED DATA AT 25°

Substance	Formula	Mol. wt.	Density	$-\Delta U_B$ kcal. mole^{-1}	$-\Delta U_R$ kcal. mole^{-1}	$-\Delta H_R$ kcal. mole^{-1}	$-\Delta H_f^\circ$ kcal. mole^{-1}	d ΔU_R/dT mole^{-1}, cal.
Fumaric acid	$C_4H_4O_4$	116.071	1.635	319.75 ± 0.05[a]	319.30 ± 0.09[b]	318.71	194.88	−14
Maleic acid	$C_4H_4O_4$	116.071	1.59	325.21 ± .04	324.73 ± .09	324.14	189.45	−15
α-d-Glucose	$C_6H_{12}O_6$	180.154	1.544	670.17 ± .07	669.58 ± .13	669.58	305.73	−65
α-d-Glucose hyd.	$C_6H_{14}O_7$	198.169	1.56	667.37 ± .12	666.73 ± .18	666.73	376.90	−71
β-d-Glucose	$C_6H_{12}O_6$	180.154	1.54	(671.67)[c]	(671.08)[c]	(671.08)[c]	(304.23)[c]	−65
Succinic acid	$C_4H_6O_4$	118.087	1.56	356.99 ± .04	356.54 ± .08	356.24	225.66	−27

[a] These values are the precision uncertainties. [b] These values include an allowance for a 10% uncertainty in the Washburn correction. [c] These values calculated from solution data.

Huffman[19] have calculated for the reaction α-dextrose(s) = β-dextrose(s) at 25°, $\Delta F = 400$ cal. This leads to a value for β-dextrose(s) of $\Delta F^\circ = -218{,}320$ cal. The values of the free energies of these six compounds and the other essential data are collected in Table III. For the entropies of the elements we have used for C, H_2 and O_2 the values 1.36,[20] 31.23,[21] and 49.03[22] e. u. per mole, respectively.

TABLE III

THERMAL DATA AT 298.1 °K.

Substance	$\Delta H^\circ_{298.1}$, kcal.	$S_{298.1}$, ke. u.	$\Delta S_{298.1}$, e. u.	$\Delta F^\circ_{298.1}$, kcal.
Fumaric acid	−194.88	39.7	−126.3	−157.23
Maleic acid	−189.45	38.1	−127.9	−151.32
Succinic acid	−225.66	42.0	−155.2	−179.36
α-d-Glucose	−305.73	50.7	−291.9	−218.72
α-d-Glucose (hyd.)[a]	(−376.52)	(60.4)	(−338.0)	(−275.76)
β-d-Glucose[a]	(−304.23)	(54.4)	(−288.2)	(−218.32)

[a] The data for these two substances are calculated from solution data as described in the text.

Using the calculated values of ΔF° and ΔH_f° for α-dextrose hydrate and β-dextrose in conjunction with the equation $\Delta F = \Delta H - T\Delta S$ we have calculated ΔS and S for these two substances. The entropy values thus calculated have been included in Table III.

Summary

1. The experimentally determined heats of combustion at 25° of fumaric acid, maleic acid, α-dextrose and α-dextrose hydrate are presented.

2. Using the data of this paper and certain other data the free energies of formation at 25° of fumaric acid, maleic acid, succinic acid, α-dextrose, β-dextrose and α-dextrose hydrate have been calculated.

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(19) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York City, 1932, p. 179.

(20) Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).

(21) Giauque, *ibid.*, **52**, 4816 (1930).

(22) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

PASADENA, CALIF. RECEIVED APRIL 8, 1938

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Ionic Dissociation of Sodium Triphenylmethyl

BY ELIJAH SWIFT, JR.

It has been shown[1] that the sodium derivatives of certain free radicals may behave as electrolytes in solution. Bent[2] has taken advantage of this fact in calculating the electron affinity of triphenylmethyl in his studies of the strength of bonds in organic compounds. In order to make this calculation, he was forced to assume a value for the ionization constant of sodium triphenylmethyl, since no direct measurements were available. The value used was 10^{-4}, but the statement was made that this value is somewhat uncertain, and that the true value is probably considerably lower than this.[3]

Subsequent to the publication of this calculation, Kraus and Fuoss[4] discovered a relationship between the dissociation constants of weakly dissociated salts in solvents of low dielectric constant and a parameter *a* which is roughly proportional to the distance of closest approach of the ions in solution. If we assume from crystal

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(1) (a) A. W. Schlenk and E. Marcus, *Ber.*, **47**, 1664 (1914); (b) C. A. Kraus and W. H. Kahler, THIS JOURNAL, **55**, 3541 (1933).

(2) H. E. Bent, *ibid.*, **52**, 1498 (1930).

(3) See footnote 14; H. E. Bent and R. G. Gould, *ibid.*, **57**, 1218 (1935).

(4) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 1022 (1933).

data[5] that the radius of the triphenylmethide ion is 4.6 Å. and that of the sodium ion is 1.0 Å., a distance of closest approach of 5.6 Å., corresponding roughly to a is obtained. The dissociation constant calculated from this value by the equations of Kraus and Fuoss is approximately 9×10^{-10}. The true value may be expected to be larger, due to solvation effects in solution. On the other hand, the calculation assumes that the charge is, on the average, centrally located, rather than at one end of the molecule on the methyl carbon atom. If this is not the case, then the dissociation constant will be smaller.

The discrepancy between this estimate of the ionization constant and that assumed by Bent is so great that it seemed of interest to determine the true value if possible. Moreover, a value so different from the one assigned by Bent would affect the calculated value of the electron affinity of triphenylmethyl by several kcal. It should be possible to determine the true value of the dissociation constant by conductance measurements if it is of the order of 10^{-4}, since Kraus and Hawes[6] have determined the dissociation constants of compounds of about this strength by that means. Consequently, an investigation of the conductance of ethereal solutions of sodium triphenylmethyl was undertaken as the best solution of the problem.

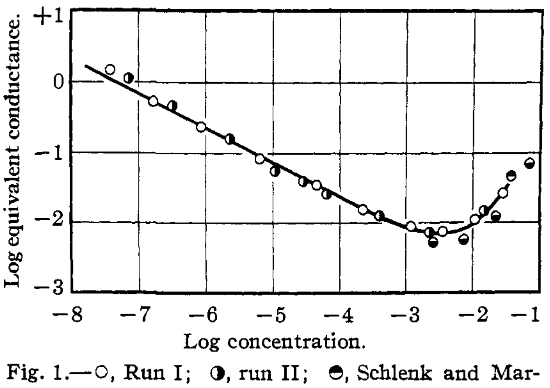

Fig. 1.—○, Run I; ◑, run II; ◓, Schlenk and Marcus; ◒, Ziegler and Wollschitt.

Bent and Keevil[7] have described the method of measurement used for the extremely high resistances encountered. The solutions were prepared and diluted according to the technique described by Bent and Dorfman.[8] The triphenylchloromethane used in the preparation of the solutions was analyzed and found to be at least 99% pure. The specific conductance of the solvent ether was measured and found to be approximately 9×10^{-12}, and a correction for this was applied to the more dilute solutions.

Two sets of determinations at 25° were made, the concentrations measured lying between 10^{-1} and 10^{-8} moles per liter. Measurements at lower concentrations than 10^{-8} were found to be unreliable due to adsorption on the platinum plates of the cell, cumulative errors in dilution, and the difficulty of obtaining accurate measurements of the resistance, which was of the order of 10^9 ohms.

TABLE I

Run I		Run II	
C, moles/liter	Equivalent conductance	C, moles/liter	Equivalent conductance
2.84×10^{-2}	0.0253	1.49×10^{-2}	0.01471
1.08×10^{-2}	.0107	2.18×10^{-3}	.00780
3.62×10^{-3}	.00775	3.37×10^{-4}	.0125
1.19×10^{-3}	.00865	6.72×10^{-5}	.0262
2.21×10^{-4}	.0159	2.79×10^{-5}	.0405
4.37×10^{-5}	.0344	1.05×10^{-5}	.0670
6.37×10^{-6}	.0875	2.16×10^{-6}	.160
8.37×10^{-7}	.238	3.09×10^{-7}	.414
1.67×10^{-7}	.516	6.90×10^{-8}	1.08
2.58×10^{-8}	1.74		

Errors in measurement, as deduced from random scattering of the points from the best curve that could be drawn through them, amounted usually to less than 2%, except at extreme dilution.[9] The single measurement of Schlenk and Marcus[1a] at 20° falls very close to the curve, in contrast to the measurements of Ziegler and Wollschitt[10] at 0°, which show a difference of approximately 20% from these measurements, well outside the experimental error of these measurements. This difference cannot be due to a difference in temperature, since the temperature coefficient of the conductance between 0 and 25° in this range of concentration was measured and found to be smaller than the experimental error. Hydrolysis of the sample of triphenylchloromethane used would have lowered the values of the equivalent conductance, and cannot explain the fact that the values obtained here are above those of Ziegler and Wollschitt.

There is a very definite minimum shown by the log equivalent conductance–log concentration curve, which according to the theory of Kraus and Fuoss is caused by the formation of triple

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(5) The diameter of the triphenylmethide ion is calculated from the density of triphenylmethane, the diameter of the sodium ion from X-ray analysis of sodium chloride.

(6) C. A. Kraus and W. W. Hawes, THIS JOURNAL, **55**, 2776 (1933).

(7) H. E. Bent and N. B. Keevil, *ibid.*, **60**, 193 (1938).

(8) H. E. Bent and M. Dorfman, *ibid.*, **57**, 1924 (1935). See also Ref. 2.

(9) See also Ref. 7 for discussion of errors in the measurements.

(10) K. Ziegler and H. Wollschitt, *Ann.*, **479**, 123 (1930).

ions.[11] Below the minimum the curve shows a slope almost exactly equal to $-{}^1/_2$, corresponding to a dissociation into two ions. It is this latter equilibrium which is of interest to us here.

In order to calculate the dissociation constant from these data, it is necessary to know the value of the limiting conductance. This can be calculated by mathematical extrapolation of the curve by the method of Kraus and Fuoss[12] if the measurements are carried out at sufficiently low concentrations. However, in solvents of extremely low dielectric constant, such as ether ($\epsilon = 4.3$), there is not sufficient ionization at attainable concentrations to allow the application of this method. It was therefore impossible to use an exact method here, and only an approximation can be made.

In the first place, if the value of the dissociation constant used by Bent (10^{-4}) is used to calculate the limiting conductance from data just below the minimum, a value of 0.03 is obtained. These measurements show values of the equivalent conductance which are greater than this, and consequently it must be inferred that the value 10^{-4} is considerably too high, as predicted by Bent.[3]

An estimate may be made by using Walden's rule on the results of Kraus and Kahler,[1b] who measured the conductance of sodium triphenylmethyl in liquid ammonia. Assuming that the limiting conductance in liquid ammonia is 175 from an inspection of their curve, the limiting conductance in ether at 25° would be 200, if no other effect than that of viscosity is considered. Using this value to compute K, we obtain 1.5×10^{-12} from points on the linear portion of the curve. This is probably a maximum value because of the factors considered below.

In the first place, the estimate of the limiting conductance in ammonia may be too low, due to a reaction which tended to depress the conductance at the lower concentrations. Second, Walden's rule should be applied only with the greatest caution in solvents where there may be some solvation of the ions considered.[13] Kraus[14] has shown that there is considerable solvation of the alkali metal ions in liquid ammonia, which is probably due to coördinate bond formation, the nitrogen furnishing the electrons. Although ether possesses the necessary unshared electron pairs to form such bonds, it is doubtful if they are formed to any great extent. Thus, in an analogous case, ammonia acts as a strong base in the presence of protons, while ether is an extremely weak base. Moreover, ether has a weak external field due to the screening effect of the ethyl groups on its dipole. Thus a higher value of the mobility of sodium ion in ether than would be estimated by Walden's rule should probably be taken, with a corresponding decrease in the ionization constant.

Assuming a value of the ionization constant of 1×10^{-12} we may calculate the effect on the electron affinity of the free radical. The value for ΔF_2 for the reaction $Na + R = Na^+ + R^-$ is found to be $-7.$ kcal., instead of -17.9 as previously estimated.[15] This increases the value of ${}^1/_2\,(\Delta F_5)$[16] for the reaction ${}^1/_2\,(R_2 + 2Na = 2Na^+ + 2R^-)$ from -15.15 kcal. to -4.3 kcal., and the value of the electron affinity of triphenylmethyl becomes -48 ± 5 kcal. instead of -59 ± 5 kcal.

It is of some interest to note that the value of the dissociation constant for sodium triphenylmethyl calculated by the equations of Kraus and Fuoss is considerably higher than the value estimated by the use of Walden's rule. Recalculating the value of a from the dissociation constant 1×10^{-12} gives a value of a equal to approximately 4 Å., instead of 5.6 Å., the value obtained from crystal data, assuming the charge to be at the center of the ion. It is, of course, questionable to attribute physical significance to a, although it is probably closely related to the effective dipole length of the associated ion pair. It would be anticipated, from resonance phenomena, that the charge is, on the average, distributed over the whole ion, due to the continuous shifting of the electrons throughout the aromatic ring structure. Either this is not the case here—which is highly improbable—or else the close approach of the sodium ion polarizes the triphenylmethide ion and reduces the effective separation of the charges.

The author wishes to thank Professor H. E. Bent, who suggested this problem and who was most generous with his time during the course of the work.

Summary

1. The conductances of dilute solutions of so-

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[11] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 2387 (1933).

[12] C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 476 (1933).

[13] For example, the value of the ionic mobility times the viscosity of the solvent for Na^+ in water is 0.45, in liquid ammonia it is 0.34, for K^+ the values are 0.66 and 0.42.

[14] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1027 (1933).

[15] Reference 2, Equation 2.

[16] Reference 2, p. 1503, Equation (2) should be labelled (5).

dium triphenylmethyl in ether have been measured.

2. A value for the ionization constant of this compound is found and the methods of estimating it are discussed.

3. The effect of this value on the value of the electron affinity of triphenylmethyl is calculated. The revised value is -48 ± 5 kcal.

CAMBRIDGE, MASS. RECEIVED APRIL 6, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION, GENERAL MOTORS CORPORATION]

The Induced Liquid Phase Decomposition of Hydrocarbons

BY PAUL L. CRAMER

The induced decomposition of hydrocarbons by means of known free radical producing compounds has been studied by a number of investigators. These reactions with various hydrocarbons, carried out in both the vapor and liquid phase, have been initiated by the thermal and photochemical decomposition of small amounts of metal alkyls and aryls, azo compounds, ethylene oxide, aldehydes, ethers, and ketones. The vapor phase induced decomposition of *n*-butane[1] gave the normal thermal reaction products. Similar results have been obtained with *n*-pentane at high reaction pressures.[2] The induced decomposition of other gaseous paraffins has been reported.[3] The report by Echols and Pease that ethane is inert when compared with propane and butane in such induced reactions is in accord with certain data presented in this paper. Similar gaseous phase reactions with the olefins have been reported only for ethylene.[4] The induced ethylene reaction in benzene solution has been described.[5] Other induced liquid phase reactions of hydrocarbons are included in a recent literature review.[6]

In a previous paper[5] the author reported on the thermal decomposition of relatively large amounts of tetraethyllead in solution in various types of hydrocarbons; however, only the results for benzene and for benzene in the presence of ethylene and hydrogen were described in detail. The purpose of the present paper is to describe the liquid phase decomposition of relatively large amounts of tetraethyllead in a number of liquid paraffinic, olefinic, aromatic, and hydroaromatic hydrocarbons. The hydrocarbons used in these experiments were *n*-heptane, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, *n*-decane, cyclohexane, 1-hexene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 3,3-dimethyl-1-butene, 1-heptene, 2,3,3-trimethyl-1-butene, diisobutylene, cyclohexene, benzene, naphthalene, tetrahydronaphthalene, and decahydronaphthalene. These experiments were carried out in a bomb at reaction temperatures of 200 to 300°. The course of the reaction was followed by a complete analysis of the gaseous reaction products, and in certain cases the oily liquid reaction products were examined.

Contrary to a recent statement in the literature[6] that "no solvent has yet been discovered which is inert to free radicals," the aromatic hydrocarbons, benzene and naphthalene, appear to be quite inert to the decomposition products of tetraethyllead at temperatures below 300°. Induced reactions were obtained with all of the paraffins, olefins, and hydroaromatics included in this study. The apparent type and extent of the reactions appear to be determined largely by the class and the molecular structure of the hydrocarbon.

In contrast to the vapor phase reactions, the conversion products formed in the liquid phase consist entirely of high boiling hydrocarbons. This fact is a great aid in determining the probable course of the decomposition products of tetraethyllead free from the interference of any gaseous reaction products of the hydrocarbon itself. For the comparison of the results obtained with different hydrocarbons, the liquid phase method has certain disadvantages. Due to the differences in vapor pressure, the concentration of tetraethyllead varies appreciably with various hydrocarbons. Although the reaction temperatures are comparable for any class of hydrocarbons, it varies considerably with different classes.

As previously proposed,[5] the liquid phase reactions may best be explained by assuming that

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(1) Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

(2) Unpublished data from this Laboratory.

(3) Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929); Echols and Pease, *ibid.*, **58**, 1317 (1936).

(4) Taylor and Jones, *ibid.*, **52**, 1111 (1930); Rice and Sickman, *ibid.*, **57**, 1384 (1935).

(5) Cramer, *ibid.*, **56**, 1234 (1934).

(6) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).