The Heat of Dissociation of the CarbonCarbon Linkage

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The Heat of Dissociation of the Carbon-Carbon Linkage

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(Received May 4, 1933)

Ziegler's colorimetric measurements of the dissociation of hexaphenylethane provide information in regard to ΔF and ΔH for this process in solution. Assuming that ΔS for the dissociation of other similar compounds is approximately the same and independent of the temperature (over a short range), ΔF and ΔH of dissociation of a variety of compounds have been calculated from published data.

It is suggested that the effects of substitution are approximately additive. There is evidence to indicate that the heat of activation of the association reaction of free radicals is very low; if this is the case the heats of dissociation estimated from the calculations of this paper provide information in regard to the heat of activation of the dissociation reaction.

THE heat of dissociation of the carbon-carbon linkage in simple aliphatic compounds such as ethane can be estimated from heats of combustion and an estimation of the heat of sublimation of carbon. The most probable value seems to be between 70 and 80 kg cal. If the six hydrogen atoms of ethane are substituted by six aryl groups such as the phenyl group, the resulting compound, hexaphenylethane, spontaneously dissociates in solution into the free radical triphenylmethyl. This and related phenomena have been extensively studied since the first discovery of triphenylmethyl by Gomberg more than thirty years ago. It is the purpose of this paper to summarize what quantitative data are available in regard to the dissociation of substituted ethanes and the free radicals containing trivalent carbon. We have been particularly interested in this laboratory[1] in the effect of alkyl groups (C_nH_{2n+1}) on the degree of dissociation of substituted ethanes, and have studied some years ago a variety of substituted dixanthyls all of

which have the general formula
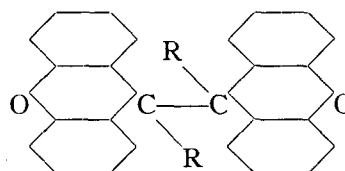
in which R may be either a hydrogen atom, an alkyl group, or an aryl group.

The most satisfactory work on the quantitative study of the dissociation of a compound into free radicals is that of Ziegler[2] who studied by a colorimetric method the degree of dissociation of hexaphenyl ethane in a variety of solvents. He also studied the dissociation at two different temperatures and thereby calculated the heat of dissociation. I shall use his measurements as a starting point for my calculations. Equilibrium constants at 293°K obtained by Ziegler for the dissociation of hexaphenylethane varied from 1.2 to 19.2 depending on the nature of the solvent. Expressing his results in terms of mole fractions,

[1] J. Am. Chem. Soc. **47**, 3068 (1925); **48**, 1743 (1926); **49**, 2080 (1927); **51**, 1925 (1929).

[2] Ziegler, Ann. **373**, 163 (1929).

the free energy of dissociation ΔF°_{293} varies from 6.8 kg cal. to 5.3 kg cal., the values of ΔH°_{293} from his own measurements vary from 10.5 kg cal. to 12.0 kg cal. Taking the mean of each of these results we may estimate that $T\Delta S$ for the process is equal to about 5 kg cal. which in turn gives the value of ΔS as about 17 e.u. It seems reasonable to assume that the same entropy change may be involved in the formation of other free radicals by the dissociation of a carbon-carbon linkage, at least in solution in organic solvents. We shall therefore assume that this value is independent of the substituents attached to the two carbon atoms which dissociate from each other. We shall further assume that over the range of temperatures necessary in the extrapolations to be employed the value of ΔS is essentially independent of temperature; we may thus calculate ΔF°_{298} from ΔF at some higher temperature by the approximate equation

$$\Delta F^\circ_{298} = \Delta F^\circ_T + 17(T - 298).$$

Various methods may be employed for estimating ΔF°_T at different temperatures; none of these methods are particularly accurate and the estimates are certainly in error by as much as ± 1.0 kg cal. Such errors, however, are not serious since Ziegler's results show that variations in ΔF and ΔH of as much as 1 or 2 kg cal. may occur due to the nature of the solvent. Therefore, all the values with which we are dealing in this paper may be regarded as uncertain within at least ± 1 kg cal. In spite of their approximate nature, however, we believe that a comparison of all the quantitative facts now available may be of some service in connection with various theories which have been developed on the effect of substituents on the energy of binding of one carbon atom to another.

In Table I are summarized the calculations based on the assumptions previously mentioned. The table is divided into two parts. The first deals with the dixanthyl series which has been particularly studied in this laboratory. The facts on which these computations are based have been previously recorded in the papers referred to. The second part of the table deals with what may be called the tetraphenyl series. The information in regard to these compounds and some others has been exceedingly well summarized in

Walden's monograph[3] from which the data have been taken. The method of estimating the degree of dissociation in all but one case depends either on a determination of the apparent molecular weight by the freezing point method in some solvent (usually molten naphthalene at 353°K) or by roughly estimating colorimetrically the temperature at which the degree of dissociation is about 1 percent. The method of estimating α is given in the next to the last column of the table. The value of ΔF°_T is given in the final column. The value of ΔF°_{298} is calculated from this value on the assumption of a constant entropy change as previously explained, and the value of ΔH°_{298} is assumed to be 5 kg cal. greater than ΔF°_{298}.
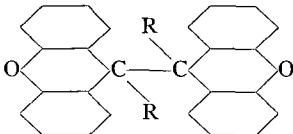
The method of estimating the values for dixanthyl (R = H) requires special comment and the values are very much less certain than the others. The value of ΔF°_{298} was estimated from the fact that the rate of oxygen absorption at 483°K was approximately the same as that for dibutyldixanthyl at 298°K.[4] This rate was presumably a measure of the rate of dissociation of the free radical since this has been proved to be the case with the alkyl derivatives (Conant and Evans). Taking the value of the unimolecular rate constant as 10^{-2} and E as 35 kg cal. (the value found for dimethyldixanthyl), the value of the constant for the rate of dissociation at 298° may be estimated as 10^{-11}. If we further assume that the rate of association of a series of related free radicals is nearly independent of their structure, we may estimate that the value of K (the dissociation constant) for dixanthyl is 10^9 less than for dibutyldixanthyl (since the rate constant of dissociation of the latter is 10^{-2}). The value of ΔF°_{298} of dissociation of dixanthyl may be estimated therefore as 12.3 kg cal. greater than the value for ΔF°_{298} for dibutyl dixanthyl; this gives $13.4 + 12.3 = 25.7$. This value is, of course, a very rough estimate based on several assumptions which are probably only approximately valid.

In connection with Table I it should be noted that the standard state is taken as that of a

[3] P. Walden, *Die Chemie der Freien Radikale.*
[4] J. B. Conant and B. S. Garvey, Jr., J. Am. Chem. Soc. **49**, 2084 (1927); J. B. Conant and M. W. Evans, J. Am. Chem. Soc. **51**, 1932 (1929).

TABLE I. *Estimated values of ΔF and ΔH of dissociation.*

R	ΔF°_{298} kg cal.	ΔH°_{298} kg cal.	Method of estimating α	ΔF°_T kg cal.
(a) Dixanthyl Series of General Formula				

R	ΔF°_{298} kg cal.	ΔH°_{298} kg cal.	Method of estimating α	ΔF°_T kg cal.
C_6H_5 $C_6H_4CH_3$	3.6	8.6	m.w. at 353°	2.7
ClC_6H_4	3.9	8.9	m.w. at 353°	3.0
$(CH_3)_2CH$	qualitatively estimated to be about the same as C_6H_5			
$C_6H_5CH_2$	11.5	16.5	color. ($\alpha = .01$ at 373°)	10.2
$n.\ C_3H_7$ $n.\ C_4H_9$	13.4	18.4	color.($\alpha = .01$ at 433°)	11.1
CH_3 C_2H_5	15.5	20.5	color.($\alpha = .01$ at 483°)	12.4
H	25.7*	30.7*	458°* (O_2 absorption)	
(b) Tetraphenyl Series of General Formula $(C_6H_5)_2C$—$C(C_6H_5)_2$ with $\begin{smallmatrix} \vert & \vert \\ R & R \end{smallmatrix}$				
C_6H_5	5.5†	10.5†	m.w. at 353°	4.6
$\alpha\ C_{10}H_7$	1.6	6.6	m.w. at 301°	1.6
$\beta\ C_{10}H_7$	3.9	8.9	m.w. at 353°	3.0
$p.\ CH_3OC_6H_4$	3.7	8.7	m.w. at 326°	3.2
$o.\ CH_3OC_6H_4$	3.4	8.4	m.w. at 326°	2.9

* See text for explanation of method of calculation.

† Direct colorimetric equilibrium measurements of Ziegler (Ann. **373**, 163 (1929)) give ΔF_{293} 5.3–6.8 and ΔH 10.5–12.0, from which $T\Delta S = 5$ and $\Delta S = 17$ e.v., the values used in the other calculations in this table as explained in text.

hypothetical supercooled liquid of such a nature that it forms an ideal solution with the solvents in question. The interesting question of the relation between the values of ΔF and ΔH referred to this basis and referred to the gaseous state we prefer to leave open at present. Whether or not a large correction would have to be made for the difference in the energy effects of solvation of the free radical and ethane seems to us still somewhat uncertain. It is conceivable that a solvation phenomenon is involved in the formation of the free radicals. If this is not the case, however, the correction from our standard state to the gaseous state would probably not exceed a few kg cal. At all events, the numbers which are given in Table I may be used for predicting the behavior

of organic compounds in a variety of solvents including, in the case of liquid substances, the pure liquids themselves.

The results given in Table I enable us to estimate the effect of various substituents on the tightness of the carbon-carbon linkage. If such effects are approximately additive we may deduce from the data of Table 1 the effect caused by the replacement of a single hydrogen atom in ethane by a single group. The difference in the dixanthyl series between phenyl and hydrogen is 22 kg cal. This refers to the difference caused by the replacement of the *two* hydrogen atoms of dixanthyl by *two* phenyl groups. Therefore, the effect for a single phenyl group may be estimated as 11 kg cal. In a similar way the other values of Table II are obtained from Table I. It is very

TABLE II. *Estimated values of effect of substituent groups on heat of dissociation of the ethane linkage.*

Substituent R	Change in ΔH_{298} of dissociation of ethane caused by replacement of one hydrogen atom by *single* group (kg cal.)
Methyl, ethyl (CH_3-, C_2H_5-)	-5
Higher normal alkyl groups (e.g., C_4H_9-)	-6
Sec. and tert. alkyl groups (e.g., $(CH_3)_2CH-$)	-11
Phenyl (C_6H_5-)	-11
Benzyl ($C_6H_5CH_2-$)	-7
Alpha-naphthyl ($\alpha\ C_{10}H_7-$)	-13
Beta-naphthyl ($\beta\ C_{10}H_7-$)	-12
$p.$ Methoxyphenyl ($p.\ CH_3OC_6H_4-$)	-12

interesting that if we take the value for phenyl as 11 and the observed value for ΔH of dissociation of hexaphenyl ethane (10.5) we may estimate the heat of dissociation of the carbon atoms in ethane as $6 \times 11 + 10.5 = 76.5$ kg cal. This is in excellent agreement with the most probable values determined from thermal data.

When a value of 76 is taken for the heat of dissociation of ethane itself and the values for the single groups given in Table II it is interesting to predict the heat of dissociation of certain compounds which cannot at present be measured. Tetraphenylethane has a value of 32 and pentaphenylethane 21. The value for the latter compound is about that of dimethyldixanthyl and the

value for the tetraphenyl compound somewhat greater than that of dixanthyl itself. One would predict that the pentaphenyl compound should give some evidence of dissociation when heated and the tetraphenyl compound probably would not. This is indeed the case,[5] as has been known for some time. On the other hand, hexamethylethane may be calculated as having a value of $\Delta H°_{298}$ of dissociation of 46 kg cal. This is such a large value that it seems unlikely that this compound would show any evidence of dissociation between the central carbon-carbon linkage even at a fairly high temperature. As a matter of fact, cracking experiments in this laboratory have shown that the compound decomposes around 500° but with the formation of methane and other products; there is no evidence of a cleavage of the central carbon-carbon linkage.

The close similarity between the secondary and tertiary alkyl groups on the one hand and the aryl groups on the other has been frequently referred to in papers from this laboratory. The behavior of tetracyclohexyl-diphenyl-ethane recently prepared by Marvel[6] is further evidence in this direction. Although this compound does not form any measurable quantity of free radical in solution, its reactions indicate clearly that a small amount of dissociation takes place.

In the calculation of ΔF of dissociation for dixanthyl itself, it was assumed that the rate of association of all free carbon radicals was approximately the same. There are a great many qualitative facts in the literature which make this assumption probable. The rate of dissociation of ethanes has been measured in two instances. In the case of hexaphenyl ethane itself the work of Ziegler[7] indicates that the heat of activation of the dissociation reaction is almost the same as that of $\Delta H°$ for the process. In other words, the association reaction has almost no heat of activation. The results in the dixanthyl series point in the same direction. The heat of activation of the dissociation of dimethyl-dixanthyl and diethyl-dixanthyl, for example, is about 30 kg cal. and the value for di-n-butyl-dixanthyl is about 26. A

comparison of these numbers with the values of $\Delta H°_{298}$ in Table I indicates a heat of activation for the association reaction of 14 to 8 kg cal. The measurements are not sufficiently accurate to make these numbers very significant, but it seems extremely probable that the heat of activation of the association reaction in both hexaphenylethane and dixanthyl is small. If this is in general the case, it is clear that the values of the heat of dissociation will give us some information in regard to the heat of activation for the dissociation process in a variety of compounds. Where the value of $\Delta H°$ is less than 12, we may expect clear evidence of the dissociation by means of the color and the peculiar reactions such as rapid oxygen absorption. Where the values run from 15 to 20 a slow oxygen absorption may be expected as well as a reaction with sodium amalgam. The speed of these reactions may very often be simply a measure of the rate of formation of the free radical,—as has been shown to be the case in at least two instances. For values of $\Delta H°_{298}$ of dissociation between 20 and 30, oxygen absorption or decomposition with cleavage of the carbon-carbon linkage may be expected to take place when the compound is heated to 450 or 550°K. On the other hand, with values as high as 46 kg cal. it seems quite clear that other modes of decomposition might take place before the cleavage of the two central carbon atoms occurs. It would, of course, be a matter of great interest to have available such substances as hexaisopropylethane or even tetraisopropyl-diethylethane. These compounds should undergo appreciable dissociation at room temperature. Unfortunately, all attempts to prepare these compounds or substances from which they might be prepared have hitherto failed.

In conclusion it may be mentioned that no account has been taken in this work of the effect of unsaturated groups on the ease of dissociation of the carbon-carbon linkage. There is a mass of qualitative evidence to show the effectiveness of such groups but the data did not lend themselves to the estimations which have been made.[8] Similarly the interesting question of the difference be-
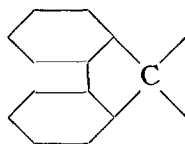
[5] Reference 3, p. 75.

[6] Marvel, J. Am. Chem. Soc. 52, 2976 (1930).

[7] Conant and Evans, reference 4 and Ziegler, Ann. 479, 277 (1930).

[8] See for example: Davis and Marvel, J. Am. Chem. Soc. 53, 3840 (1931).

tween two phenyl groups and the phenylene group

has been left untouched. The phenylene group is much less effective in promoting dissociation than two phenyl groups, whereas the dixanthyl group is somewhat more effective. We may estimate roughly the effect on $\Delta H°_{298}$ for these two *divalent* groups as 18 and 23, respectively. These numbers are to be compared with 22 for the corresponding two phenyl groups. Among the facts which any theory in regard to the dissociation of the carbon-carbon linkage must explain is the difference in these numbers.

I should like to express my indebtedness to my colleague Professor H. E. Bent with whom I have often had the pleasure of discussing the problems considered in this paper.