estrogenic activities determined in order to relate their activities to the size and character of the groups R and R′.

For characterization their benzoates have been made.

BALTIMORE, MD. RECEIVED MARCH 31, 1944

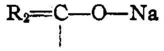
---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

# Single Bond Energies. V. The Association of Ketyls

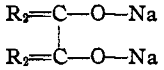
BY H. E. BENT AND A. J. HARRISON[1]

The compound formed by the addition of an alkali metal to an aromatic ketone is highly colored and by some investigators[1a] has been assigned the formula



$$R_2{=}\underset{|}{C}{-}O{-}Na$$

although evidence has been advanced[2] to show that the compound should not be considered to be a free radical but is associated and should be represented as a pinacolate



$$\begin{array}{l} R_2{=}C{-}O{-}Na \\ \qquad | \\ R_2{=}C{-}O{-}Na \end{array}$$

We have attacked this problem by the method used in studying hexaphenylethane and triphenylmethyl reported by Ziegler and Ewald.[3] They found that on diluting a solution of hexaphenylethane the deviations from Beer's law could be explained satisfactorily by assuming an equilibrium between the ethane and the free radical and also assuming only the free radical to be colored.

Benzophenone was chosen as the first compound to be studied since it is the simplest aromatic ketone. Fluorenone was chosen as the second compound due to the presence of a five-membered ring. Peculiarities in five-membered rings have been found in the acidity of very weak acids,[4,5] the dissociation of free radicals[6] and the addition of sodium to single bonds.[7]

A solution of the ketyl is prepared by shaking the ketone in ether solution with 0.6% sodium amalgam. A portion of this solution is used to rinse the apparatus, removing adsorbed water. Fresh solution is then poured into the cell in which the optical density is to be determined. In order to avoid the errors inherent in an analysis one sample is used for a whole series of measurements, dilution being accomplished by means of the apparatus shown in Fig. 1. This device is carefully calibrated to determine the amount of hold up in the annular space when a solution is poured through it. The total volume of ether is determined at the beginning of the experiment. This permits one to pour a known fraction of the solution through the dilution device and then to distill the ether back, condensing it in the solution which had been retained in the annular space, thus diluting the solution by a known fraction. Two or three dilutions may be carried out with one cell before the solution becomes too dilute to measure with precision. Another sample of the solution is removed and the sodium determined analytically.

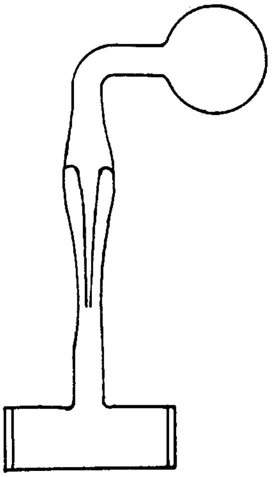


Fig. 1.—Dilution device. The solution is diluted without exposing to air by inverting the whole apparatus. A certain fraction of the liquid is retained in the annular space around the capillary. The apparatus is then returned to its original position without pouring solution back from the flask. On cooling the cell solvent distills from the flask back into the cell.

Measurements of the optical density were carried out with a spectrophotometer, previously described,[8] which illuminates the cell with monochromatic light and gives high precision. All cells were of Pyrex glass with fused plane glass windows mounted in Dewars.

The experimental results from the study of fluorenone indicate that it gives rise to a ketyl which obeys Beer's law within the accuracy of our experimental measurements. A series of measurements at room temperature gave ratios for the optical densities which agreed very closely with the values for the dilution ratio. In order to find evidence for association if possible at lower temperatures a series of dilutions were carried out, measurements being made at −112°, using solid carbon disulfide as the cooling agent. These measurements also showed close agreement with Beer's law. Since one would expect a temperature coefficient for the process of dissociation which would greatly increase the frac-

---

(1) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Missouri. This paper was presented at the spring meeting of the American Chemical Society at Detroit in 1943.

(1a) Schlenk, *et al.*, *Ber.*, **44**, 1183 (1911); **46**, 2840 (1913); **47**, 473 (1914).

(2) Bachmann, THIS JOURNAL, **55**, 1179 (1933).

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

(4) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

(5) McEwen, *ibid.*, **58**, 1124 (1936).

(6) Conant, *J. Chem. Phys.*, **1**, 427 (1933).

(7) Bent and Keevil, THIS JOURNAL, **58**, 1367 (1936).

(8) Jacobsohn, Bent and Harrison, *Rev. Sci. Inst.*, **11**, 220 (1940).

tion dissociated at room temperature as compared with −112°, we may conclude that this compound exists essentially 100% in the form of a free radical at room temperature.

On lowering the temperature of a solution of this ketyl there is an increase in the molecular extinction coefficient which by itself might be taken as evidence for dissociation! The series of dilutions at the lower temperature, however, give no such evidence. Examination of the absorption curve indicates that the percentage change in the molecular extinction coefficient is not constant on lowering the temperature but depends upon the wave length, there being an increase in the maximum and a narrowing of the band. Hence one is not justified in taking the value of the molecular extinction coefficient at infinite dilution at one temperature and using this with values at other temperatures to calculate the fraction dissociated.

The results with benzophenone are perhaps more interesting but unfortunately somewhat less trustworthy. On dilution, the solution does not obey Beer's law and as one would predict from this observation, there is a large temperature coefficient for the optical density. Contrary to the observations on fluorenone there is no change which is larger than our experimental error in the shape of the absorption curve, over the more limited range of 20°. In this case we would be justified in using a value of the molecular extinction coefficient of the pure ketyl as calculated from data at one temperature to determine the fraction dissociated at another temperature. The temperature coefficient is so large that the range of measurement did not need to exceed that from 0 to 20°.

Many dilution series gave deviations from Beer's law which could not be explained by the simple assumptions made at the beginning of this paper. In practically every case the dilute solution was darker than could be accounted for by any experimental error or by the dissociation of the pinacolate into the free radical. We are inclined to believe that in these series some excess ketone was present, produced by hydrolysis, the ketyl reacting with minute traces of water firmly held on the glass apparatus even after evacuating and washing with ketyl solution. We have observed that the addition of ketone to the ketyl does destroy the blue color. If one assumes that an unstable compound is formed containing one molecule of ketone and two of ketyl, possibly forming a chelate ring, it is possible to account for our experimental data quantitatively. The possible presence of the disodium derivative of the ketone has been considered but can be ruled out by a consideration of the difference between the absorption curves for the mono- and the di-sodium derivatives. The strong maximum for the latter at a wave length of 510 is sufficiently far from the wave length used of 630 to permit one to say from a study of the latter curve that only an extremely small amount of the disodium derivative could have been present.

In some series of dilutions, especially those carried out with fresh solutions which had been in contact with the glass for too short a time to react with much water, the deviations from Beer's law could be quantitatively accounted for by a simple equilibrium between pinacolate and free radical. Using these runs alone values have been calculated for the equilibrium constant.

The results on the two ketyls mentioned above are not what one would predict from a consideration of the behavior of similar hydrocarbon free radicals. The relatively small association of triphenylmethyl as compared with phenylfluoryl indicates that the removal of two hydrogen atoms and the connection of two benzene rings by a carbon–carbon bond favors association. In the study of the ketyls described in this paper the effect is just the opposite.

The explanation of this apparent inconsistency is probably to be found in the assumption that phenylfluoryl has more resonance than triphenylmethyl. The converse has usually been assumed in accounting for phenylfluoryl being less stable as a free radical than triphenylmethyl.[9] If one considers the symmetry of the free radical alone one would be led to this conclusion. If on the other hand we assume that phenylfluoryl has more resonance, then we must also assume that the greater tendency to associate is due to a smaller amount of steric hindrance. This is in accord with the observation of Cline[10] that diphenyldifluoryl can be hydrogenated with much less ease than hexaphenylethane, indicating a smaller amount of steric hindrance in the undissociated molecule. The hydrogenation experiment gives an answer to the question of steric hindrance without the complication of resonance which appears in the process of dissociation to give a free radical.

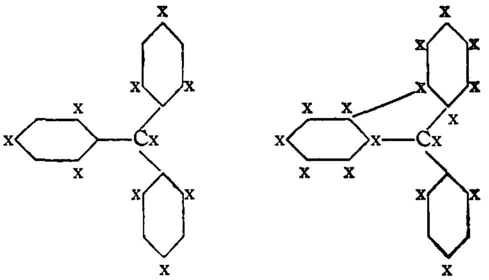
The details of the way in which this extra resonance appears in the free radical phenylfluoryl have been suggested to one of the writers by R. W. Stoughton. It is evident from the illustration below that whereas the odd electron can appear on only alternate carbon atoms in triphenylmethyl, in phenylfluoryl the odd electron can appear on every carbon of the fluoryl group and hence we have a much larger number

---

(9) Pauling and Wheland, *J. Chem. Phys.*, **1**, 373 (1933), have concluded that one can give a reasonable explanation for a smaller amount of resonance in the fluoryl radical and thus explain the smaller amount of dissociation without recourse to steric hindrance. Muller and Janke, *Z. Elektrochem.*, **45**, 386 (1939), come to similar conclusions. No experimental data were available in 1933 to suggest the need of any other explanation. The data of Muller and Janke do not agree with ours on the two ketyls under consideration. Although it is true that Muller and Janke were working in more concentrated solutions it seems hardly likely that this would reverse the relative ease of dissociation of the two compounds.

(10) H. E. Bent and J. E. Cline, THIS JOURNAL, **58**, 1626 (1936).

of resonating structures. A double bond appears between two rings in some cases.



We will now summarize the above discussion and then proceed to indicate the way in which our conclusions aid in understanding the peculiarities of five-membered rings referred to in the third paragraph of this paper. Our conclusions based upon evidence given above is that two phenyl groups attached to a single carbon differ in two important respects from the fluoryl group. In the first place the removal of two hydrogen atoms and the connection of the rings by a single bond produces a more compact group and reduces the probability of steric hindrance. In the second place the formation of a five-membered ring makes possible an increase in the stability of the group on account of the resonance resulting from an odd electron (or resulting from a free pair of electrons) taking up every position in each ring.[11]

As we will see, sometimes one and sometimes both factors are important in a given chemical reaction.

Taking up first a case where only steric hindrance is involved we consider the oxygenation of hexaphenylethane and diphenyldifluoryl. Resonance does not concern us in this reaction since the initial and final products are hydrocarbons involving no special resonance of the type found in free radicals. We would expect steric hindrance to weaken the carbon–carbon bond in the former compound more than in the latter and thus to cause more heat to be liberated in the former case than in the latter. The difference of 15 kcal. experimentally measured by Cline is in accord with this explanation.

An illustration involving chiefly resonance and little steric hindrance is that of the ketyls discussed in this paper. One cannot say with certainty that steric hindrance is of no importance but one would hardly expect it to be of great importance on account of the relatively small size of the O–Na group as compared with a benzene ring. If then resonance is of primary importance in determining the behavior of ketyls we would expect that the ketyl from benzophenone would dissociate slightly as compared with the ketyl derived from fluorenone. Experimentally, we have shown in this paper that this is the case, sodium fluorenone being entirely dissociated under conditions which give rise to only partial dissociation of sodium benzophenone.

Turning now to a case in which both factors are of significance we find an excellent illustration in the dissociation of hexaphenylethane and diphenyldifluoryl. We might expect that the greater steric hindrance in hexaphenylethane promoting dissociation would be offset by the greater resonance in phenylfluoryl. Actually we find that these two factors nearly compensate each other so that experimentally the difference is only about 8 kcal. as estimated by Conant,[6] leading to greater dissociation of hexaphenylethane. Subtracting this from the 15 kcal. difference for the heat of oxygenation gives 7 kcal. for the excess resonance of two phenylfluoryl radicals as compared with two triphenylmethyl radicals, or 3.5 kcal. for the difference between phenylfluoryl and triphenylmethyl.

A similar situation is to be found in the addition of sodium to hexaphenylethane and to diphenyldifluoryl. Here we might expect steric hindrance to favor the addition to the former compound and resonance to favor addition to the latter. Since steric hindrance is found to be more important than resonance in the case of simple dissociation, we might expect the same to be the case with the addition of sodium. Experimentally, Keevil[7] has shown that sodium adds more readily to the diphenyldifluoryl than to hexaphenylethane. This fact may be accounted for by bringing in the additional fact that in diethyl ether solution the sodium compounds are not dissociated into ions but exist as ion pairs. This indicates that the smaller ion will give rise to the more stable ion pair and hence sodium will react more readily with diphenyldifluoryl than with hexaphenylethane.[12]

Another way of expressing the same idea is to say that we are dealing here with a situation analogous to that described under hydrogenation. In the case of hydrogenation only steric hindrance was involved as no free radical was produced as a final product. Here, in the addition of sodium, we may be justified in saying that steric hindrance is of little if any significance compared with resonance which occurs in the negative ion. The reason for saying that steric hindrance may be of little or no importance here is that, although present in one molecule of the reactant it is also present in both molecules of the product and hence tends to cancel out.

Finally, a very striking example from the work of Conant and Wheland is to be found in the relative acid strengths of triphenylmethane and phenylfluorene. The essential reaction involved in those experiments is the substitution of a

---

[11] Resonance in an ion is to be treated in the same way as in the corresponding free radical as pointed out by Wheland, *J. Chem. Phys.*, **2**, 479 (1934).

[12] One might expect to find a sodium to carbon distance which would determine the stability of the ion pair, but Kraus and Hawes have shown, THIS JOURNAL, **55**, 2784 (1933), that this is not the case. Rather, it is the total size of the ion which determines the value of "*a*" of closest approach and hence the stability of the ion pair.

proton by an alkali metal ion. The inference based upon the foregoing discussion would be that steric hindrance would not be a factor in the acid where the hydrogen atom is localized on a single carbon but that it would be a factor in the ion pair formed as the product of the reaction and that it would operate in the same direction as resonance rather than against it as in one of the earlier examples. Thus we would expect from both of these factors that phenylfluoryl would behave as though it were a stronger acid than triphenylmethane. Experimentally, Conant and Wheland[4] have shown that it behaves as though it were stronger by a factor of $10^7$. A revision of this value by McEwen[5] in extending the work of Conant and Wheland increases the value from $10^7$ to $10^{12}$. This would correspond to a free energy value of about 15 kcal. This is in the direction one would expect from resonance but larger than would be predicted by resonance alone. At least part of this difference is doubtless due to smaller steric hindrance in the ion pair.

## Experimental

Experimental precautions have been discussed in previous papers of this series dealing with similar procedures. A high vacuum technique was employed to avoid contamination with air or water vapor. The ketones were purified, the ethyl ether distilled from a solution of sodium fluorenone and decomposition of ether avoided during sealing off from the vacuum line by condensing the ether vapor. The solution of the ketyl is found to be quite stable, a sample having been kept for more than a year without appreciable decomposition or change in color; sunlight and temperatures of 40° produce no appreciable decomposition. Nevertheless we sometimes observed a decrease in the optical density of solutions during rather short intervals of time. We attribute this to small amounts of water liberated from the rather large surface of glass exposed to the solution during the dilution experiments.

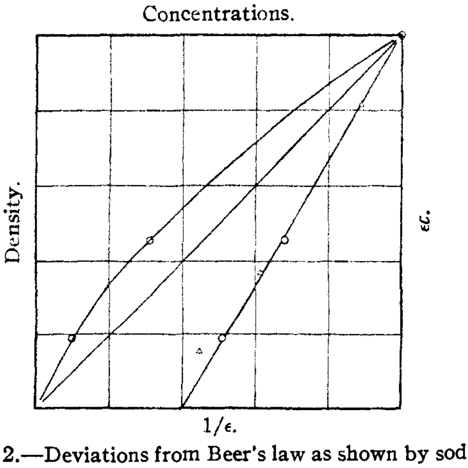


Fig. 2.—Deviations from Beer's law as shown by sodium benzophenone.—Top curve is calculated from the equilibrium constant and the value of $\epsilon_\infty$. The points are experimental, only two of the three being required to evaluate $K$ and $\epsilon_\infty$. Middle curve is what one would expect from Beer's law. Bottom curve is drawn through the experimental points, illustrating the way in which deviations from Beer's law can be expressed by a straight line. The triangles are for another series of measurements made on an older solution.

Typical experimental results on sodium benzophenone are shown in Fig. 2, the concentration scale being arbitrary. The straight line through the origin is drawn in to illustrate the behavior of the solution if it obeyed Beer's law. The experimental points, falling above this straight line, indicate the deviations from Beer's law which may be accounted for by the dissociation of the pinacolate. The third curve, which is a straight line, has been drawn to a different scale for convenience in calculating values proportional to the equilibrium constant and the molecular extinction coefficient of the ketyl. The scale used in the plot of the third curve follows from the discussion: If we let (R) represent the concentration of the free radical and ($R_2$) the concentration of the pinacolate then

$$K = (\mathrm{R})^2/(\mathrm{R}_2) = \frac{2(\epsilon/\epsilon_\infty)^2C}{1 - (\epsilon/\epsilon_\infty)}$$

in which $C$ is the mole fraction of solute expressed as ketyl, $\epsilon_\infty$ is the molecular extinction coefficient of the pure free radical and $\epsilon$ is the apparent molecular extinction coefficient defined by the expression $\log I_0/I = \epsilon Cl$. $I_0/I$ is the ratio of light intensities and $l$ is the length of the cell expressed in centimeters. The ratio $\epsilon/\epsilon_\infty$ gives the fraction of the material dissociated. The above expression for the equilibrium constant may be transformed into the more convenient expression

$$\frac{1}{\epsilon} = \frac{2\epsilon C}{\epsilon_\infty 2K} + \frac{1}{\epsilon_\infty}$$

which is the equation of a straight line if we plot the reciprocal of the apparent molecular extinction coefficient against the product of the molecular extinction coefficient and the concentration. The intercept gives the molecular extinction coefficient at infinite dilution and the slope gives, in combination with the intercept, the equilibrium constant. Actually, before we analyzed the solutions to determine the concentration we plotted the concentration, in arbitrary units, divided by the optical density against the optical density. The final analysis, giving the concentration, gives the appropriate factor for converting the equilibrium constant and the molecular extinction coefficient into absolute values.

The analysis of the solution was accomplished by extracting the ether solution with small portions of 0.5 $N$ hydrochloric acid. This hydrolyzes the ketyl and gives an aqueous solution of sodium chloride. The method of McCance and Shipp[13] permits the determination of quantities of sodium of the order of 0.05 mg. Since we are dealing with very dilute solutions it seemed best to use a method capable of handling quantities of this order of magnitude. Subsequent experiments have shown our solutions to contain considerably larger quantities of sodium which would have made possible a more precise determination of the concentration. The optical density changes with time, but by standardizing the procedure and taking a measurement with the spectrophotometer one hour after the formation of the red color, results were obtained which indicate a possible accuracy of perhaps one or two per cent.

The results obtained with benzophenone, using only those series which give evidence by the straightness of the $1/\epsilon$ against $\epsilon C$ plot that hydrolysis was unimportant, give values of $K$ of $4 \pm 1 \times 10^{-5}$ and for $\epsilon_\infty$ of $7 \pm 2 \times 10^3$ when concentrations are converted into moles per liter. The calculation of the heat of the reaction may be carried out in a variety of ways, the most obvious of which is to calculate from dilutions at two temperatures two values of the equilibrium constant. This method gives results not too far out of line with the value reported below but probably is not as good a procedure as to take a solution of a given concentration quickly from the higher to the lower temperature. The possibility of reaction with water on the glass is minimized by this method and probably the results are more reliable. If one takes the change in

---

[13] McCance and Shipp, *Biochem. J.*, **25**, 449 (1931).

optical density and calculates a value for the heat of the reaction assuming the associated material to be constant one obtains as a minimum value for the heat the quantity 3.3 ± 0.5 kcal. A still better method is to correct for the change in the concentration of the undissociated material using values for the equilibrium constant obtained from dilution experiments. This does not raise the value very much but leads us to report 4 ± 1 kcal. as the heat of the reaction. This value may be compared with 10 kcal. found by Ziegler and Ewald for the dissociation of hexaphenylethane.

Preliminary measurements on the sodium derivative of di-biphenyl ketone at 24 and 0° give no evidence of association at the lower temperature.

TABLE I

SODIUM FLUORENONE

| Run | Temp., °C. | Optical density | Relative concentration | Ratio of optical densities |
|---|---|---|---|---|
| 1 | 20 | 0.4076 | 1[a] | |
| | | .1716 | 0.429 ± 0.002 | 0.421 |
| 2 | 20 | .1716 | 1 | |
| | | .0711 | 0.429 | .414 |
| 3 | 20 | .3148 | 1 | |
| | | .1354 | 0.429 | .430 |
| 4 | 20 | .3006 | 1 | |
| | | .1345 | 0.429 | .447 |
| | −112 | .3751 | 1 | |
| | | (.3131 cor.)[b] | | |
| | | .1653 | 0.429 | .441 |
| | | (.1379 cor.) | | |
| 5 | 20 | .2832 | 1 | |
| | | .1224 | 0.429 | .432 |
| | −112 | .3511 | 1 | |
| | | (.2940 cor.) | | |
| | | .1496 | 0.429 | .426 |
| | | (.1250 cor.) | | |
| | | | 20° average | .429 ± 0.009 |
| | | | −112° average | .434 ± 0.008 |

[a] Actual concentration $1.21 \times 10^{-4}$ expressed as the mole fraction of the ketyl. Wave length 640 mμ. Cell length 1.4668 cm. [b] Values given in parentheses under runs 4 and 5 at −112 as "corrected" take into account the contraction of the ether on cooling from 20 to −112°. The increase in the corrected value over that found at 20° would suggest dissociation but this is not borne out by the dilution experiments. The difference is discussed in the text.

The data of Bent and Keevil[14] have been recalculated in order to obtain the value for the free energy of addition of sodium to benzophenone. As pointed out by them the existence of an appreciable amount of the ketyl in the form of the pinacolate will reduce the calculated value for the addition of sodium to the free radical. The change which we have found is scarcely of importance, the value being changed from −22.4 to −22.1 kcal., which is little more than the experimental error in the determination of Bent and Keevil.

TABLE II

SODIUM BENZOPHENONE

| Run | Temp., °C. | Mole fraction expressed as ketyl[b] $\times 10^4$ | Optical density[a] | Fraction dissociated | Equilibrium constant $\times 10^5$ |
|---|---|---|---|---|---|
| 1 | 20 | 0.540 | 0.9980 | 0.41 | |
| | | .168 | .4553 | .60 | |
| | | .052 | .1896 | .79 | 3 |
| 2 | 20 | .320 | .7498 | .61 | |
| | | .0895 | .2795 | .83 | |
| | | .0254 | .0943 | .93 | 6 |
| 3 | 20 | .400 | 1.694 | .41 | |
| | | .1732 | 0.9679 | | 3 |
| | | .154 | .9017 | .71 | |
| | | .067 | .4567 | | 5 |
| | 0 | .396 | 1.326 | .23 | |
| | | .1715 | 0.805 | | 1 |
| | | .153 | .754 | .58 | |
| | | .066 | .400 | | 2 |

[a] The optical density was measured at a wave length of 630 mμ. The equilibrium constant is expressed as a mole fraction. The cell length in runs 1 and 2 was 0.6689 cm. and in run 3 was 1.4669 cm. [b] The concentration of the ketyl at the beginning of a run is based upon an analysis of the solution for sodium. The accuracy of the determination of sodium involves an error of probably not more than 5%. However, decomposition of ketyl before the first measurement of optical density and calculations of concentrations for some of the later runs from the optical density may involve an error in concentration of as much as 30%. Inasmuch as the value for the equilibrium constant is directly proportional to the value assumed for the concentration a corresponding error is present in the equilibrium constant. The relative values of the concentration, however, are known with an error of probably not more than 1%.

## Summary

The ketyl formed by treatment of fluorenone with sodium amalgam gives no evidence of associating to a pinacolate at either room temperature or −112°.

The shape of the absorption curve for sodium fluorenone is a function of temperature which rules out as a general procedure the using of a molecular extinction coefficient at one temperature in calculating with precision the fraction dissociated at another temperature.

Benzophenone forms a ketyl with sodium in ether solution which is associated at room temperature to a large extent to form a pinacolate. The dissociation constant for this reaction is found to be $4 \pm 1 \times 10^{-5}$ at 20°, concentrations being expressed as mole fractions.

Sodium benzophenone in ether solution has an apparent molecular extinction coefficient which decreases rapidly as the temperature is lowered. Combining such data with dilution experiments at 0° enables one to calculate a temperature coefficient for the dissociation constant and a corresponding heat of dissociation of 4 ± 1 kcal.

COLUMBIA, MISSOURI RECEIVED JANUARY 17, 1944

---

[14] H. E. Bent and N. B. Keevil, THIS JOURNAL, **58**, 1368 (1936).