[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. XI. The Free Energy of Addition of Sodium to Ketones and Unsaturated Hydrocarbons

BY HENRY E. BENT AND NORMAN B. KEEVIL

The previous paper of this series[1] describes a potentiometric method for determining the free energy change associated with the addition of sodium to an organic compound. The method has been tested on reactions involving the addition of sodium to several free radicals by comparing the value obtained by the potentiometric method with the value obtained by an analysis of the equilibrium mixture. In order to determine whether or not the potentiometric method may be used in studying other types of compounds, namely, ketones and unsaturated hydrocarbons, the investigation of these reactions by a direct analysis of the equilibrium mixture has been undertaken. In a later paper we hope to compare these results with the results by the potentiometric method. The data are interesting in themselves and shed light on the structure of ketyls.

The experimental procedure is essentially that described in earlier papers of this series.[2] The equilibrium is approached from both sides and the concentrations of the reactants and products determined by analysis. The activity of sodium in the amalgam is adjusted to give a reaction which is approximately 50% complete.

Purification of Materials

Benzophenone was purified by fractional distillation under reduced pressure. The product was recrystallized twice from absolute methyl alcohol, giving large white crystals which melted at 47.7°.

Fluorenone obtained from Eastman Kodak Company was recrystallized from 95% alcohol and stored in a desiccator. The melting point was raised from 180-182 to 183°.

Dibiphenyl ketone, synthesized from phosgene and *p*-bromobiphenyl, melted at 229°.

Tetraphenylcyclopentadienone was prepared in connection with work reported in the fourth paper of this series.

Tetraphenylethylene was very kindly supplied by Mr. E. L. Martin. After recrystallization it melted at 220-221°.

Stilbene and anthracene were used as supplied by Eastman Kodak Company.

Ether was stored either over sodium benzophenone prepared from sodium-potassium alloy, or over sodium fluorenone prepared from dilute amalgam. The latter method of drying the ether does away with the hazard associated with the use of sodium-potassium alloy.

Experimental Results

Benzophenone.—The experimental results are recorded in Table I. Some difficulty was encountered due to the fact that the ketyl sometimes precipitated and was not easily dissolved by repeated washing with solvent. In the latter runs the volume of the solution was considerably increased in order to avoid this precipitation. The equilibrium constant refers to the reaction $(C_6H_5)_2CO + Na = (C_6H_5)_2CONa$. (When we have information on the amount of pinacolate present we will recalculate our results if this becomes necessary.) The concentrations of the ketone and ketyl may be expressed in any units. The activity of the sodium is referred to the pure metal as the standard state. In runs 11 to 15 the ketyl was prepared by shaking benzophenone with 40% amalgam. This leads to the formation of the disodium derivative which was then poured onto a slight excess of ketone, forming the monosodium derivative.[3] This change is accompanied by a change in color from the clear purple of the disodium derivative to the blue of the monosodium derivative. The solution of the monosodium derivative was then poured onto mercury and shaken until equilibrium was established. In run 18 the ketyl was prepared by shaking the ketone with a saturated amalgam (about 1%). Run 13 was carried out at 0° and the rest at 25°. In run 16 benzene was the solvent. The solubility of ketyl in ether seems to be about 10^{-5} moles per liter and in benzene about 5×10^{-3} moles per liter. Exact values cannot be given due to the tendency of the solution to supersaturate, and the slowness with which the precipitate dissolves. The last four runs are probably the best. In approaching the equilibrium by adding sodium directly to the ketone an amalgam was used in which the mole fraction of sodium was 0.0008.

Fluorenone forms a monosodium derivative. The insolubility of the ketyl again introduced some experimental difficulties. In order to avoid error from possible precipitation during the reac-

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[1] Bent and Keevil, THIS JOURNAL, **58**, 1228 (1936).

[2] Dorfman, *ibid.*, **57**, 1455 (1935).

[3] When the monosodium derivative was prepared by this indirect method the amount of ketone at equilibrium was obtained by evaporation of the solution to dryness and correcting for the amount of ketyl determined by titration.

TABLE I

EQUILIBRIUM DATA ON BENZOPHENONE-SODIUM

No.	Direction of approaching equilibrium	Moles Na in mercury	Moles of Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
11	Removal of Na	6.72×10^{-5}	6.08×10^{-4}	0.2561	0.3399	8.08×10^{-4}	22.3
12	Removal of Na	4.08×10^{-5}	1.708×10^{-4}	.2088	.3964	5.17×10^{-4}	22.0
13[a]	Removal of Na	1.83×10^{-5}	2.296×10^{-4}	.2531	.4609	7.20×10^{-4}	20.7
14	Removal of Na	8.54×10^{-7}	2.81×10^{-5}	.1977	.4671	2.64×10^{-4}	23.6
15	Removal of Na	6.59×10^{-6}	1.30×10^{-4}	.2557	.3854	2.64×10^{-4}	23.4
16	Removal of Na	1.79×10^{-4}	1.23×10^{-3}[b]	.3560	.2635[b]	1.79×10^{-4}	23.2
22	Addition of Na	1.27×10^{-5}	9.02×10^{-5}	.1153	2.275	3.40×10^{-4}	22.2
23	Addition of Na	7.33×10^{-4}	2.265×10^{-4}	1.3181	2.135	2.170×10^{-4}	22.1
24	Addition of Na	2.172×10^{-5}	1.38×10^{-4}	0.229	1.067	3.36×10^{-4}	22.5
18	Removal of Na	5.34×10^{-5}	5.33×10^{-5}	2.066	2.104	3.70×10^{-4}	22.7
						Average of all results at 25°	22.7
						Average of last four	22.4
			Data on Benzophenone-Potassium				
17	Addition of K	4.17×10^{-5}	2.80×10^{-4}	0.7515	0.880	2.80×10^{-4}	27.8

[a] Temp. = 0°. [b] Benzene as solvent.

TABLE II

EQUILIBRIUM DATA ON FLUORENONE-SODIUM

No.	Direction of approaching equilibrium	Moles Na in mercury	Moles Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
11	Removal of Na	2.81×10^{-6}	6.71×10^{-4}	0.4308	0.4659	5.07×10^{-4}	24.9
12	Removal of Na	4.27×10^{-6}	6.64×10^{-4}	.3906	.4202	6.13×10^{-4}	24.4
13	Removal of Na	3.05×10^{-6}	3.40×10^{-4}	.6767	.2544	4.83×10^{-4}	24.7
14	Removal of Na	2.22×10^{-4}	3.59×10^{-4}	2.8344	2.0708	1.0×10^{-5}	25.3
21	Addition of Na	1.34×10^{-5}	5.60×10^{-5}	.6600	2.448	1.0×10^{-5}	25.0
23	Addition of Na	3.17×10^{-6}	2.54×10^{-4}	.2973	2.281	1.77×10^{-4}	24.6
24	Addition of Na	4.88×10^{-7}	1.41×10^{-4}	.2550	1.684	2.80×10^{-4}	25.0
						Average	24.8

TABLE III

EQUILIBRIUM DATA ON DIBIPHENYL KETONE

22	Addition of Na	3.78×10^{-4}	1.99×10^{-4}	0.7043	2.175	1.14×10^{-5}	23.8
23	Addition of Na	3.44×10^{-4}	1.86×10^{-4}	.6784	1.659	2.0×10^{-6}	24.8
24	Addition of Na	6.40×10^{-5}	1.64×10^{-4}	.3368	2.078	3.0×10^{-5}	23.7
25	Addition of Na	2.99×10^{-5}	1.51×10^{-4}	.6760	1.882	3.47×10^{-5}	24.4
17	Removal of Na	3.71×10^{-5}	4.30×10^{-5}	3.103	1.756	6.59×10^{-5}	24.0
18	Removal of Na	7.45×10^{-5}	7.23×10^{-5}	3.1518	2.073	1.04×10^{-4}	23.7
						Average	24.1

tion the concentration of ketone was determined by evaporation of the solution to dryness after titration of the sodium as in the case of benzophenone. The various runs are of unequal importance due to the fact that in some cases the concentration of one of the reactants was very low. The large negative value for ΔF for the reaction of addition of sodium to these ketones necessitates working with very dilute amalgams. These ketones exhibit about the greatest stability which can be studied by this method.

Dibiphenyl Ketone.—This ketone behaved in much the same way as the two discussed above, forming a monosodium derivative. In preparing the ketyl for removal of sodium with dilute amalgam a saturated amalgam was used.

Tetraphenylcyclopentadienone.—This ketone is remarkable in that it adds more than one equivalent of sodium even when shaken with very dilute amalgam. The rate of addition of sodium, however, is very slow and we were not able to add as much as two equivalents of sodium even after shaking the ketone with 40% amalgam for fifteen days.

Tetraphenylethylene.—This unsaturated hydrocarbon and the two following compounds exhibit a much smaller tendency to add sodium than any compounds which we have studied hitherto. The sodium derivatives are so unstable as to be completely decomposed by a saturated sodium amalgam. They might be studied by means of solid sodium amalgams but probably better still by means of the potentiometric method. We will

TABLE IV

PRELIMINARY DATA ON UNSATURATED COMPOUNDS

Compound	No.	Procedure	Moles Na in mercury	Moles Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
Tetraphenylethylene	1	Out with mercury	2.15×10^{-4}	2.80×10^{-6}	0.3645	0.4413	1.48×10^{-4}	30.2
Tetraphenylethylene	2	Out with mercury	2.49×10^{-4}	3.42×10^{-6}	.6258	.5903	1.77×10^{-4}	30.5
Tetraphenylethylene	3	Out with 1% amalgam	6.61×10^{-3}	1.15×10^{-5}	.7553	.5913	1.96×10^{-4}	28.0
Tetraphenylethylene	4	Out with 1% amalgam	7.72×10^{-3}	6.1×10^{-6}	.1471	.886	2.60×10^{-4}	24.3
Stilbene	1	Out with 1% amalgam	3.29×10^{-3}	2.80×10^{-5}	.0552	.2793	1.66×10^{-4}	24.8
Stilbene	2	Out with 1% amalgam	4.28×10^{-3}	2.84×10^{-5}	.0801	.6572	6.9×10^{-5}	25.5
Anthracene	1	Out with mercury	3.35×10^{-4}	6.10×10^{-6}	.3513	.6134	9.21×10^{-4}	13.7
Anthracene	2	Out with 1% amalgam	8.96×10^{-3}	7.12×10^{-5}	.1787	.9397	4.55×10^{-4}	12.4

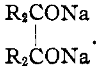
reserve comment on these compounds until we have more exact quantitative data. The results reported in Table IV are of interest in indicating the most negative value which ΔF can assume. These are minimum values only, the true value lying nearer to zero. The reaction to which ΔF refers is $2Na + (C_6H_5)_2C{=\!=}C(C_6H_5)_2 = (C_6H_5)_2CNaCNa(C_6H_5)_2$.

Stilbene.—Saturated amalgam did not remove as much of the sodium in the case of stilbene as it did with tetraphenylethylene. It is possible, therefore, that the value in the last column of the table is the correct value for this compound. Since we have not approached the equilibrium from both sides, however, it is safer to consider this a maximum value for $-\Delta F$.

Anthracene.—This compound is remarkable in that it is an unsaturated hydrocarbon and yet differs from the two just discussed in that it will combine with one atom of sodium. This reaction we hope to investigate further and until we have quantitative data will reserve further comment. The values given in the last column of the table are again maximum values for $-\Delta F$. They are approximately half of those given for the two previous compounds since only one atom of sodium is involved and the reaction is written $Na + C_{14}H_{10} = NaC_{14}H_{10}$.

Discussion of Results

The free energy data reported indicate that fluorenone combines with sodium more readily than dibiphenyl ketone, which in turn combines with sodium more readily than benzophenone. This is not the order in which the groups attached to the carbonyl group are effective in promoting dissociation of ethanes but is the order in which free radicals containing these groups combine with sodium. It therefore appears that the problem is not a simple one and that there must be at least two factors involved. It is doubtless too early to state these factors with certainty but since the facts can readily be explained by two factors which must be of importance one is tempted to suggest an explanation. In the first place we will assume that the addition of sodium first forms a free radical, the sodium being attached to the oxygen to give a molecule of the formula $R_2\underset{|}{C}ONa$. Such a molecule will have a stability which is determined partly by resonance.[4] We would, therefore, expect dibiphenyl ketone to combine more readily with sodium on account of the greater resonance energy of the biphenyl group. In the case of fluorenone, however, we must look for another explanation. Bachman has presented evidence to show that these free radicals double up to form pinacolates of the formula



$$\begin{array}{c} R_2CONa \\ | \\ R_2CONa \end{array}$$

. This reaction will not affect the above argument involving resonance if the sodium addition compound is largely in the form of the pinacolate. In the case of fluorenone, however, another factor must be considered. The data on the heat of oxidation and hydrogenation of hexaphenylethane[5] indicate that steric hindrance is an important factor in determining the stability of free radicals. The large association of phenylfluoryl may therefore be due to the fact that the tying together of the two benzene rings decreases the steric hindrance and gives rise to a more stable bond. If this be assumed then it is easy to see why fluorenone combines more readily with sodium than the other ketones. The decreased steric hindrance results in the formation of more pinacolate which removes the product of the reaction and therefore shifts the equilibrium in the direction of formation of the ketyl.

The next point to be discussed is the location of the sodium atom in the ketyl molecule. Recently Wooster[6] has considered the possibility of

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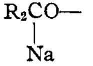
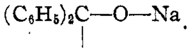
[4] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[5] Bent, Dorfman, Cuthbertson and Leary, THIS JOURNAL, **58**, 165 (1936); *ibid.*, **58**, 170 (1936).

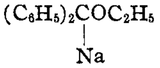
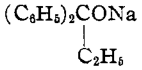
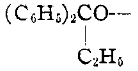
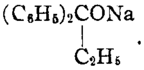
[6] Wooster, *ibid.*, **57**, 112 (1935).

the sodium being attached to the carbon, forming an oxygen free radical of the formula  $R_2CO{-}\,|\,Na$ Our experimental results lead us to the conclusion that the sodium is attached to oxygen and not to carbon. If we compare the free energy of addition of sodium to carbon and to oxygen we find that there is a large difference which is in favor of sodium being attached to oxygen. Thus sodium may be readily removed when attached to carbon free radicals by dilute sodium amalgam while we were not able to remove even a trace of sodium from the oxygen free radical derived from 9-chloro-10-phenanthrol with the aid of mercury.[7] This indicates that the free energy of addition of sodium to a free radical is at least 5 kcal. more negative in the case of the oxygen free radical. Hence we conclude that sodium is much more firmly attached to oxygen than to carbon and that therefore the ketyl should be represented as a carbon free radical with the sodium on the oxygen  $(C_6H_5)_2C{-}O{-}Na$.

Another entirely different approach to the problem leads to the same conclusion. Thus the negative ion formed from the ketyl can be represented by the structures $(C_6H_5)_2C:\underset{..}{\ddot{O}}:$ and $(C_6H_5)_2\underset{..}{C}:\underset{..}{\ddot{O}}\cdot$ in which the odd electron may be either on the carbon or the oxygen. Many other structures would have to be included to form the complete wave equation, these structures involving quinonoid rings. The ion must be considered to be the sum of all of these structures with, however, a preponderance of the structure of lowest energy. Since the electron affinity of oxygen is greater than that of carbon,[8] we may expect the first structure given above to be that of greatest importance. This corresponds to the negative charge being localized on the oxygen and hence would lead to an ion pair in which the sodium is attached to oxygen. Finally, a third factor which promotes the addition of sodium to oxygen is to be found in the coulomb interaction of the sodium ion and the electrons which may be considered to give rise to resonance in the molecule as a result of their wandering around in the benzene rings. This coulomb interaction will tend to localize an electron pair in the vicinity of the sodium atom.[9] Here we find a pronounced difference in the effect of such a pair being localized on the carbon or on the oxygen. If the pair is localized on the oxygen the odd electron on the carbon is still free to wander. On the other hand, if the pair is localized on the carbon the free electron on the oxygen is not free to wander and hence this structure would be less stable on account of the smaller amount of resonance energy in the molecule.

The above three lines of evidence lead us to the conclusion that the sodium is attached to oxygen in the ketyl. No shift of the sodium is then required in forming the double molecule.[10]

If our point of view is correct the question arises as to what is the probable answer to each of the lines of evidence which Wooster brings out, leading to the opposite conclusion.

Wooster's first evidence arises from the fact that  $(C_6H_5)_2COC_2H_5\,|\,Na$ does not rearrange to give the compound  $(C_6H_5)_2CONa\,|\,C_2H_5$ and he therefore concludes that the initial product of the reaction of sodium-benzophenone with ethyl bromide is the free radical  $(C_6H_5)_2CO{-}\,|\,C_2H_5$ and that this reacts with a second molecule of ketyl to give  $(C_6H_5)_2CONa\,|\,C_2H_5$. We agree that a reaction of the oxygen free radical with sodium benzophenone would be expected as our experiments have shown that sodium cannot be removed from an oxygen free radical by mercury while it can be removed very readily from sodium benzophenone. This difference is due in large measure to the fact that when the sodium is removed from the ketone a single bond between oxygen and carbon is changed into a double bond and it is this process which permits the sodium to be removed so readily from the ketone. Wooster's suggestion that because the ethyl group adds to carbon the sodium must originally have been on the carbon does not seem conclusive in the absence of other evidence. We quite agree with Wooster, however, that the course of the alkylation may be determined by a configuration which is not that of the normal molecule and in this case may be that in which the charge is on the carbon.

The second evidence presented by Wooster has to do with the relative ionization of sodium benzhydrylate, sodium benzophenone and sodium triphenylmethyl. Wooster informs us that he

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(7) Bent, Dorfman and Bruce, THIS JOURNAL, **54**, 3250 (1932).

(8) Glockler, *Phys. Rev.*, **46**, 111 (1934).

(9) There seems to be no way at present of estimating the magnitude of this effect. We hope to study this problem in more detail experimentally.

(10) Bachman, THIS JOURNAL, **55**, 1179 (1933).

expects in the near future to give a different interpretation of these data so that this argument no longer concerns us here. Recent correspondence indicates that Wooster's views and ours are not in complete accord. The question of the degree of localization of the sodium ion in the ion pair is answered by the data of Kraus and Fuoss on the compounds C_6H_5ONa (2.70), C_6H_5SNa (4.95) and $C_{10}H_7ONa$ (2.9–3.1). The values given in parentheses are for the distance "a," multiplied by 10^8, which is characteristic of the distance of closest approach of the two ions. It is apparent that the change from an oxygen to a sulfur atom produces a much greater change in "a," than the addition of several carbon and hydrogen atoms. We therefore conclude that in such an unsymmetrical anion the sodium is localized, in this case near the oxygen or sulfur and the anion cannot be treated as spherically symmetrical. This is the justification for the formulation of the ion pair with the sodium attached to oxygen rather than a more general formula which does not localize it at any point in the molecule.

The third line of evidence suggested by Wooster has to do with the ease with which sodium may be removed from sodium benzophenone and from sodium triphenylmethyl. Wooster gives data to show that these two compounds are about equally stable, the free energy change for the process of transferring the sodium from ketone to the free radical being within 0.5 kcal. of zero. Our data also indicate the free energy change for this reaction is small, from 0.7 to 1.0 kcal. Wooster finds that the sodium is held slightly more firmly by benzophenone while we find that triphenylmethyl has a slightly greater affinity for sodium. The difference is not significant, however, and we may consider the two sets of data in substantial agreement. Wooster concludes from these data that the sodium is attached to carbon in both cases. As we have pointed out above, however, the loss of sodium from the ketone leads to the formation of a double bond between the carbon and oxygen and therefore contributes nearly 100 kcal. to the process. If sodium were attached to carbon in both compounds we would expect (from this factor alone neglecting resonance energy) that it would be liberated from the ketone more easily by 100 kcal. This would mean that the ketyl would not be formed at all. We have calculated the heat of formation of the ketyl assuming the sodium to be on the oxygen, adding up single bond energies and estimating the magnitude of the resonance energies involved. We do not wish to present these figures in detail owing to their very rough qualitative nature, but they give the right order of magnitude for the experimental energy. When one assumes that the sodium is attached to carbon the agreement with the experimental value is very poor, as is indicated above. We, therefore, are led to the conclusion that sodium adds to the benzophenone forming a ketyl with sodium attached to oxygen which then forms a pinacolate.

Summary

1. Data are given for ΔF for the reaction of addition of sodium to benzophenone, dibiphenyl ketone, fluorenone, tetraphenylcyclopentadienone, tetraphenylethane, stilbene and anthracene.

2. The data are correlated with previous experiments which indicate the significance of resonance energy and steric hindrance.

3. Evidence is presented to show that sodium is attached to oxygen in sodium-benzophenone.

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