

funnel, the stem of which passes through the neck of a bell jar into a beaker. The crucible is washed five times with distilled water before and after filtering the manganese dioxide. The filtrate is now acidified with glacial acetic acid and 3 g. of calcium acetate added and let steam overnight. The precipitate (calcium oxalate) is collected on an alundum crucible by filtration and washed with four fillings of distilled water. The crucible and contents are now placed in a 250-cc. beaker. Ten cc. of concentrated sulfuric acid is added just before the final titration with 0.04 *N* potassium permanganate. During the titration the acid liquid is kept at a temperature of 65 to 70° and the titration with potassium permanganate continued until the rose tint remains permanent for two minutes.

Two check experiments required for each 5.94 cc. of 0.1 *N* propionic acid 18.60 and 18.60 cc., an equivalent of 7.44 of 0.1 *N* potassium permanganate.

It was found that with the above amounts of material the formation of oxalic acid was not complete with less than three hours of heating on the steam-bath. When experiments were first begun with this method the excess potassium permanganate was oxidized with hydrogen peroxide formed by the addition of sodium peroxide. All glassware used in the experiment had been cleaned with dichromate sulfuric acid cleaning mixture.

Summary

A new method has been described for the determination of propionic acid. In this method propionic acid is oxidized to oxalic acid. Such a method is especially valuable in the determination of propionic acid in the presence of formic and acetic acids.

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THE ELECTRON AFFINITY OF FREE RADICALS. IV. COMPOUNDS NOT AROMATIC HYDROCARBONS

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In the three previous papers of this series¹ values for the free energy change of the reaction of addition of sodium to eight organic free radicals have been reported and by combination with appropriate equations the electron affinities in the gaseous state calculated. These free radicals contained only phenyl, biphenyl or naphthyl groups attached to the trivalent carbon atom. The values of ΔF for the reaction²

¹ H. E. Bent *THIS JOURNAL*, **52**, 1498 (1930). **53**, 1786 (1931); Bent and Dorfman, *ibid.*, **54**, 1393 (1932).

² The standard state is the metal in the case of the sodium and for the other species the activity is taken as equal to the mol fraction.



in which R represents the free radical, were found to fall within narrow limits ranging from -17.9 kg. cal. for triphenylmethyl to -20.6 kg. cal. for tri-*bi*-phenylmethyl and within these limits the effects produced by the various groups were additive. The electron affinity in the gaseous state for these compounds was calculated to be about 60 kg. cal.

That these compounds should all give nearly the same value of ΔF for this reaction is perhaps not very surprising in view of the fact that in each case an electron is being added to an "odd" molecule to complete an electron pair. In all of the compounds heretofore studied the central atom has been carbon and the three groups attached to this carbon have been aromatic in structure. It would seem very desirable to continue the study of this reaction, extending the work to compounds of non-aromatic structure.

Unfortunately the requirements of the problem greatly limit the number of compounds which may be studied. In the first place it is essential that the ethane be either largely dissociated into the free radical or else that the equilibrium constant for this dissociation be known. If neither of these conditions is satisfied, then the addition of sodium to the ethane involves not only the free energy change of the addition of sodium to the free radical but also the unknown free energy of dissociation of the ethane. Knowing the sum of these two values and either one, the other may be calculated. From the standpoint of this investigation it is necessary to know the free energy of dissociation of the ethane or else that this be nearly complete. The converse of this calculation, the determination of the dissociation of ethanes by measuring the equilibrium with sodium, is the subject of another investigation which will be reported later.

Another very obvious requirement of this investigation is that a true equilibrium be established free from side reactions. These conditions make it impossible to study a great many of those compounds which satisfy the first condition of being largely dissociated. In some cases the solubility is too small and in others the sodium reacts with some active part of the molecule.

The free radicals reported in this paper are diphenylanisylmethyl, trianisylmethyl, pentaphenylcyclopentadienyl, pentaphenylethyl, the oxygen free radical, 9-chloro-10-phenanthroanil and the nitrogen free radical α, α -diphenyl- β -trinitrophenylhydrazyl. These compounds are known to be largely dissociated.

Diphenylanisylmethyl showed a similar behavior to triphenylmethyl and gave approximately the same value for the electron affinity. Tri-*p*-anisylmethyl and pentaphenylcyclopentadienyl failed to yield sodium derivatives that had even a slight solubility in ether and possibly these free radicals were decomposed by sodium amalgams. 9-Chloro-10-phenanthrol formed a monosodium derivative with 1% sodium amalgam but the sodium

was held too firmly to be removed by mercury sufficiently to be detected analytically. The nitrogen free radical α,α -diphenyl- β -trinitrophenylhydrazine was undoubtedly decomposed in ether by saturated sodium amalgam, even nitrobenzene being decomposed by this treatment. Pentaphenylethane reacted with sodium in liquid ammonia but failed to yield a sodium derivative that could be extracted with ether.

Experimental

Diphenylanisylmethyl.—Diphenylanisylmethylcarbinol was obtained from the Eastman Kodak Co. in the form of a brown sirup. The melting point reported for the pure carbinol is 82° .³ 7.8 g. of the sirupy carbinol was dissolved in 35 cc. of absolute ether and a little calcium chloride added. The addition of hydrogen chloride gas produced a white precipitate of the chloride. Ether was added to make a total volume of 125 cc. which dissolved the precipitated chloride and none separated upon again treating with hydrogen chloride. After standing overnight and filtering, the solution was evaporated to 30 cc. and cooled to 0° . White crystals of the chloride separated. These were crystallized twice more from ether at 0° to yield 2.4 g. of chloride melting at 123° . The value previously reported is 122° .

Anal. Calcd. for $C_{20}H_{17}OCl$: Cl, 11.50. Found: Cl, 11.54, 11.31.

The apparatus and procedure used in making the equilibrium measurements have been previously described.¹

Table I gives the experimental data for the equilibrium measurements. The column headed $\log K_2$ gives the values of the equilibrium constant for equation (1). A dissociation constant for the sodium addition compound giving ions, of 10^{-4} has been assumed here as was done in the earlier papers of this series. The dissociation constant for the ethane has been taken as 10^{-2} based upon molecular weight determinations.⁴

The mean value of ΔF is -18.3 kg. cal., which is not very different from 17.9 kg. cal., the value found for triphenylmethyl.¹

TABLE I

EQUILIBRIUM CONSTANTS FOR THE ADDITION OF SODIUM TO DIPHENYLANISYLMETHYL

G. atoms Na removed $\times 10^4$	G. atoms Na left $\times 10^4$	Moles of ether	G. atoms of mercury	$\log K_2$ $K_1 = 10^{-2}$ $K_2 = 10^{-4}$	Mean	$+\Delta F$ kg. cal.
0.613	0.854	0.138	2.70	13.54		
.279	.282	.178	2.67	13.45		
.511	1.117	.139	1.35	13.54		
.580	0.275	.169	5.05	13.23		
.727 ^a	.511	.182	3.48	13.19		
	(.520) by titration				13.4	-18.3

^a Compound treated with 40% amalgam.

The equilibrium constants obtained agree with each other as well as for any of the preceding compounds studied. However, a decided difference was noted in the color change when adding mercury. With sodium tri-

³ Gomberg and Buchler, *THIS JOURNAL*, **45**, 217 (1923).

⁴ Ref. 3, p. 220.

phenylmethyl it was possible to see a partial disappearance of the red color upon shaking with a large quantity of mercury. The ether solutions of the other compounds studied were so dark that even a ten-fold dilution could not be noted and shaking with the quantities of mercury used produced no color change that could be detected.

The ether solution obtained by treating the diphenylanisyl chloride with saturated amalgam had a red color about the same as that of sodium triphenylmethyl. A small quantity of mercury changed this to a yellow, practically the same as that of the free radical solution obtained by treating the chloride in ether solution with mercury. This apparently indicated a nearly complete removal of sodium from the addition compound for even a fifty-fold dilution of the red solution gave a color distinctly red-orange. From Table I, however, it is seen that the equilibrium constant is the same within experimental error when 1.35 mols of mercury, removing about one-third of the sodium, and 5.05 mols of mercury, removing about two-thirds of the sodium, were used. This contradiction between the evidence furnished by the color of the solution as to the amount of sodium present and that furnished by analysis, was further studied.

To test the reversibility of the color change an ether solution of sodium diphenylanisylmethyl was prepared in the usual way and decanted into a two-tube system which was then sealed off. One of these contained saturated amalgam about 1%, and the other connected to it, mercury. The red solution changed to yellow upon pouring into the mercury tube and shaking, and the original color was restored upon pouring back and shaking in the amalgam tube. This was repeated ten times with the same result, even though according to the equilibrium measurements very little sodium would be removed in the mercury tube after the first few times.

It appeared possible that a derivative containing two atoms of sodium was being formed, the red color being due to small amounts of the disodium compound and this second sodium atom being readily removed by amalgams more concentrated than those ordinarily at equilibrium with the monosodium derivative. If so this derivative should be formed completely with 40% amalgam. To test this some of the chloride was first treated in the usual way with 1% amalgam in ether solution and then poured onto 40% sodium amalgam and shaken. No deepening of the color could be noted and after decanting and shaking with mercury in the last tube, the yellow color of the previous runs was noted. Usual analyses gave the same equilibrium constant within experimental error. In addition the ether phase was hydrolyzed with water and the sodium hydroxide formed titrated. The sum of the titrations of ether and mercury phases gave 0.0001247 mole, 0.0001238 mole of chloride having been used, which agrees well within experimental error and shows that the monosodium derivative was formed quantitatively.

It appears possible that a quantity of impurity in amounts too small to affect the analytical results might be present and this form a red sodium addition compound from which the sodium is easily removed by mercury. However, an additional crystallization of the chloride this time from benzene and petroleum ether gave the same red colored solution upon treatment with 1% amalgam.⁵

Tri-*p*-anisylmethyl.—Trianisylcarbinol was made according to the directions of Baeyer and Villiger.⁶ After the sulfuric acid addition product was decomposed with water, the product was extracted with ether. A large volume of ether is needed since some of the methane tends to precipitate at this stage as an asbestos-like gummy material. The distilled product was orange-red and fragrant. It was not crystallized before oxidation^{1,7} which was followed by conversion to the picrate. This was digested with hot chloroform for half an hour and filtered by suction. It was then shaken in a mechanical shaker with a large amount of dilute alkali. On extraction with ether, desiccation over calcium chloride and evaporation, an orange oil was obtained which solidified on seeding with some of the solid which formed on the lip of the flask. Some of the oily carbinol was dissolved in benzene, calcium chloride added and the solution saturated with hydrogen chloride. The solution became deep red and a red precipitate formed which later turned to a red oil below the benzene. The two liquid phases were decanted from the calcium chloride and boiled down to about 75 cc. On standing for several days some deep red rosetts together with some red gum separated slowly. The clear liquid was decanted, an equal volume of absolute ethyl ether added and the solution allowed to stand overnight at 0°. Large white plate-like crystals formed which were dissolved in 30 cc. of benzene. Where the solid came in contact with air it became brick-red. When the operations were carried out in an atmosphere of carbon dioxide no marked coloration occurred. The chloride after recrystallization was washed with absolute ether several times and dried under reduced pressure over potassium hydroxide. The compound melted at 158°; that previously reported⁸ at 154–156°.

Practically no information exists about the free radical. Wieland⁹ states that the free radical tri-*p*-anisylmethyl is obtained by the splitting in ligroin of an azo compound, but he gives no description of the free radical. There are no other references to it in the literature. We obtained an orange solution with some orange precipitate upon dissolving the chloride in ether and shaking with mercury. The color disappeared upon admitting air. With a more dilute solution, 0.02 g. of chloride in 100 cc. of ether, shaken with mercury an orange solution formed without a red precipitate.

A sample of the chloride in ether was shaken with saturated amalgam. The solution became orange. After shaking for almost an hour a brown

⁵ Another possible explanation, suggested by Dr. W. L. Gilliland, is that sodium diphenylanisylmethyl exists in two tautomeric forms, one red and the other yellow or much lighter, the red existing in small amounts the sodium of which is readily removed by mercury. One would have to postulate in addition that the equilibrium between these two forms is mobile while in contact with amalgam, but not over mercury. In order to shed further light on this peculiar behavior the trianisylmethyl was studied.

⁶ Baeyer and Villiger, *Ber.*, **35**, 1197 (1902).

⁷ See also Lifschitz and Girbes, *Ber.*, **61**, 1463 (1930).

⁸ Ref. 6, p. 3031.

⁹ Wieland, *Ber.*, **55**, 1830 (1922).

suspension slowly formed and in several hours the orange color had completely disappeared.

It was thought that possibly the saturated amalgam was too strong a reducing agent and that the use of a very dilute amalgam would enable equilibrium measurements to be made.

0.614×10^{-4} mole of chloride in ether solution was shaken in a single tube carrying a stopcock with an amalgam the mole fraction of sodium in which was 0.743×10^{-4} which is about the mean concentration of the amalgams in equilibrium with diphenylanisylmethyl and its sodium derivative (see Table I). An orange colored solution together with some gray precipitate which may have been entirely sodium chloride was formed. After shaking overnight in the dark the amalgam phase was withdrawn through the stopcock and titrated. Water was then admitted to hydrolyze the ether phase and precipitate, and the mixture titrated. The orange colored solution did not change color upon adding water but was instantly decolorized by air.

To summarize the titration results

0.10×10^{-4}	mole of sodium in ether phase + ppt.
0.81	mole of sodium in amalgam after shaking
0.61	mole of sodium equivalent to Cl in original chloride
1.52	mole of sodium sum
1.46	mole of sodium in original amalgam

Considering that the end-point was not very good in titrating the ether and precipitate, these two figures check quite well.

These figures indicate that the tri-*p*-anisylchloromethane reacts quantitatively with this dilute amalgam to form the free radical but that no appreciable amount of sodium adds to the free radical to form the sodium derivative. We prepared an amalgam the mole fraction of sodium in which was 6.04×10^{-4} , about eight times as strong as the preceding one. This was done in order to force more sodium into the ether phase. In this experiment an apparatus with two tubes, similar to those used in the equilibrium measurements was used, except that the first tube also had a stopcock. 0.878×10^{-4} mole of chloride was shaken in the first tube with the amalgam. The solution turned orange and remained so upon shaking overnight in the dark. The solution was decanted and filtered into the second tube and mercury added and this shaken overnight in the dark. The orange color did not lighten after shaking with mercury, or upon admitting water, but was decolorized in air. Both phases in the second tube and the amalgam and precipitate in the first tube were hydrolyzed and titrated with the following results. The amount of sodium in the original amalgam was 3.07×10^{-4} gram atom. The amount remaining at the conclusion of the experiment was 1.93×10^{-4} gram atom. About 0.08×10^{-4} gram atom was found in the precipitate formed in the first tube. 0.88

$\times 10^{-4}$ gram atom is the amount which should be required to convert the chloride into the free radical. These amounts add up to give 2.89×10^{-4} , nearly the amount of sodium introduced in the original amalgam. This agrees with the fact that no sodium was removed by the mercury and none found in the ether phase. One may conclude, therefore, that tri-*p*-anisylmethyl may be prepared from the chloride by treatment with either mercury or an amalgam whose mole fraction of sodium is from zero to 0.7×10^{-4} . Since no sodium addition compound has been prepared, it is not possible to give a value for the free energy change for the reaction. It may be somewhat less negative than for the compounds heretofore studied.

Pentaphenylcyclopentadienyl.—This free radical has been prepared by Ziegler and Schnell,¹⁰ who found it to be completely dissociated by freezing-point measurements.

In the preparation of methylene-bis-desoxybenzoin, it was found important that desoxybenzoin should be pure, and that alkali should not be added until the formalin had been well mixed with the solution. It is desirable to cool the solution to 0° during the slow addition of alkali. Under these conditions crystals began to appear almost at once and there was no oily phase. When the reaction was carried out at room temperature, however, and the alkali added rapidly, the gummy material described by Ziegler and Schnell was obtained. Heat is liberated when the ketone is added to the final Grignard solution at the boiling point of ether, and a considerable amount of tarry by-products appeared. But when the Grignard solution was cooled to 0° and the ketone added slowly, a good yield of carbinol was obtained. This was crystallized twice from acetic acid and converted into the chloride, which melted at 170° . The value previously reported is 167° .

A sample of the chloride in ether solution was treated with 1% amalgam in the usual system. A purple colored solution was formed at first. This is the color of the free radical in benzene described by Ziegler and was also obtained by shaking an ether solution of the chloride with mercury. After shaking with the amalgam a short while, a dirty green precipitate was formed and the purple color disappeared. The ether phase remaining contained no hydrolyzable sodium.

It was thought that possibly the sodium derivative was formed but was insoluble in ether and might be soluble in benzene. The experiment was repeated using very dry benzene in place of the ether. The same phenomena occurred again although the purple color persisted longer than when in ether solution. In order to learn whether or not a more dilute amalgam would give the free radical as in the case of tri-*p*-anisylmethyl another sample of the chloride in ether solution was treated with a very dilute amalgam the mole fraction of sodium in which was 0.743×10^{-4} . Here again the same phenomena were noted, the purple solution forming at first and then a green precipitate.

The analysis of the amalgam indicated that not more than one and one-half equivalents of sodium had reacted with the chloride, one equivalent

¹⁰ Ziegler and Schnell, *Ann.*, **445**, 274 (1925).

of this being required to form the free radical. Evidently the presence of sodium amalgam catalyzes the decomposition of the free radical.

Oxygen and Nitrogen Free Radicals.—We are indebted to Professor L. F. Fieser for the 9-chloro-10-phenanthrol used in these experiments. This material had been prepared by the method of Schmidt and Lumpf and melted at 122°. The previously recorded value is 121°. ¹¹

Goldschmidt and Steigerwald¹² prepared the free radical by oxidation with lead dioxide and found it to exist in the dissociated form in several solvents.

Upon treating the phenanthrol with sodium amalgam a reaction took place which should give the same compound as would be obtained by addition to the free radical. The solution remained colorless and on shaking with mercury no sodium was removed. Ninety per cent. of the calculated amount of sodium was found in the ether solution by titration. The original phenanthrol was recovered after the titration, and identified by a mixed melting point.

This experiment clearly indicates that an oxygen-free radical unites with sodium to form a compound which is much more stable than the corresponding carbon compound. One can place the free energy change for this reaction qualitatively by saying that it is more negative than in the case of carbon by at least 5 kg. cal.

One might expect from the foregoing experiment on the oxygen-free radical that a nitrogen-free radical would show a similar behavior but would hold to the sodium less firmly. The choice of largely dissociated nitrogen free radicals is, however, very limited. α,α -Diphenyl- β -trinitrophenylhydrazyl was synthesized by the method of Goldschmidt and Renn.¹³ However, treatment of the hydrazine with the sodium amalgam resulted in side reactions which prevented further study with this compound. Doubtless the nitro groups are responsible for the various reactions observed.

We are indebted to the Milton Fund of Harvard University for financial support in this investigation.

Summary

1. ΔF for the addition of sodium to diphenylanisylmethyl is the same as for the addition of sodium to triphenylmethyl.

2. ΔF for the addition of sodium to the oxygen free radical, 9-chloro-10-phenanthroxyl, is more negative than for carbon free radicals by at least 5 kg. cal.

3. The following compounds will give no sodium addition compound when treated with a one per cent. sodium amalgam, presumably due to the

¹¹ Schmidt and Lumpf, *Ber.*, **41**, 4215 (1908).

¹² Goldschmidt and Steigerwald, *Ann.*, **438**, 202 (1924).

¹³ Goldschmidt and Renn, *Ber.*, **55**, 636 (1922).

presence of side reactions: pentaphenylcyclopentadienyl, tri-*p*-anisylmethyl and the nitrogen free radical α,α -diphenyl- β -trinitrophenylhydrazyl.

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THE HEAT CAPACITY OF SELENIUM FROM 100 TO 300°A.¹

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Previous work on the heat capacity of metallic selenium has been of a rather uncertain nature. None of the experimenters has stated the method of purification so as to have selenium free from tellurium, nor have they shown that their specimens were the metal and not some other form of selenium.

Some of the earliest work was done by Regnault.² He obtained the value 6.63 calories per mole at 98° and 5.93 at 20 to 98°. Bettendorf and Wüllner³ found 6.65 from 25 to 60°. Dewar⁴ gave the value 2.86 between liquid nitrogen and liquid hydrogen temperatures. In our investigation the selenium was carefully purified and annealed to the metallic form. The Nernst method was used to find the heat capacity.

Purification and Preparation of the Sample

A Mallinckrodt grade of selenium was dissolved in concentrated nitric acid. The selenium dioxide was then dissolved in dilute hydrochloric acid. The insoluble material was filtered out and the selenium precipitated with sulfur dioxide. The selenium came down in the red form and turned black upon drying. This was repeated twice. For the complete removal of tellurium, the method of Lenher and Kao⁵ was used, in which hydroxylamine hydrochloride was used as the reducing agent. This purification was also repeated twice. This gave a black form of selenium. The wet selenium was washed with alcohol and vacuum dried at room temperature. This amorphous selenium was then placed in a Pyrex glass tube, connected to a vacuum pump and heated. Large volumes of gas came off, and finally a tarry mass was formed. This was allowed to cool to a shiny black, brittle solid in an atmosphere of nitrogen.

The selenium was transferred to a soft glass cylinder and melted. In this was inserted two Pyrex thermocouple wells, and a spiral heating coil of No. 30 nichrome wire. (Approximate resistance was 11 ohms.) The entire assembly was then heated in an oil-bath to 210–215°, where it was kept for several hours. It was then allowed to cool slowly in a Dewar flask filled with oil of about 225°. At the end of eight hours the temperature of the oil was still about 50°, so it was assumed that only the metallic

¹ This article is an abstract of the thesis presented by L. F. Dobry to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science.

² Regnault, *Ann. chim. phys.*, [2] 73, 51 (1840); [3] 46, 281 (1856).

³ Bettendorf and Wüllner, *Pogg. Ann.*, 133, 293 (1868).

⁴ Dewar, *Proc. Roy. Soc. (London)*, 89, 158 (1913).

⁵ Lenher and Kao, *THIS JOURNAL*, 47, 2454 (1925).