concentration is reached, should lead to a slow rise in the rate. Both these factors, however, are small and do not obscure the issue.

Summary

The rate of solution of zinc cylinders, rotating in various acid solutions with depolarizers present, has been measured up to very high rotational speeds. The effect of high concentrations of sodium acetate and sodium chloride on the rate of solution of zinc and magnesium in acetic acid has been studied, and also the effect of varying acid and oxidizing agent concentrations independently.

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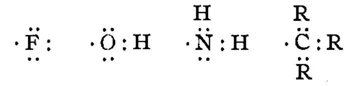
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. V. Aromatic Derivatives of Dixanthyl and *p,p'*-Biphenylene-bi-(diphenylmethyl)

BY HENRY E. BENT AND R. G. GOULD, JR.

Previous papers of this series have shown that sodium adds with about equal ease to many organic free radicals. This result was expected on account of the large electron affinity of triphenylmethyl[1] calculated in the first paper of this series.[2] Glockler[3] has shown that the electron affinity of atoms varies from −28 to +91 kcal. However, if we consider systems involving seven electrons in the outer shell we find the electron affinity remarkably constant. Thus, the values for the halogens are all of the same order of magnitude, ranging from a little over ninety kilogram calories for fluorine[3,4] to seventy-two kilogram calories for iodine.[5] Again if we consider the energy involved in adding an electron to each of the systems



$$\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\qquad \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H\qquad \cdot\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{N}}}:H\qquad \cdot\underset{R}{\overset{R}{\overset{\cdot\cdot}{C}}}:R$$

we find that the number of pairs of electrons which are shared apparently affects little the electron affinity. Fluorine gives a value of a little over ninety, OH is reported by Lederle as giving eighty-eight[6] and the value calculated by one of us for triphenylmethyl is sixty. No value is available for the NH_2 group. We have shown in previous papers of this series that all organic free radicals which we have studied have about the same electron affinity. In these compounds we have not only the same nuclear charge and the same number of shared electron pairs but also the sharing is always with another carbon atom, which in turn is attached to other carbon atoms. These considerations make it seem very probable that the differences in chemical properties of organic free radicals are not due to differences in the electron affinities of the molecules.[7]

Experimental

Phenylxanthyl Chloride.—Phenylxanthydrol was prepared by Dr. W. F. Bruce according to the directions of Gomberg and Cone.[8] The directions in the literature were followed with the modification that the xanthone was put in an extractor so that the reflux drippings from the boiling ethereal solution of the Grignard reagent slowly dissolved the ketone and carried it into the reaction flask in solution. It was pure white and melted at 159°.

Phenylxanthyl chloride was prepared by the method of Gomberg by dissolving the hydrol in benzene, adding acetyl chloride and dry hydrogen chloride gas. The phenylxanthyl chloride hydrochloride often comes down as an oil but usually turned into a dark red crystalline mass on standing. The crystals, after washing with dry benzene and petroleum ether, were suspended in dry petroleum ether and boiled until a colorless solution was obtained. On cooling, colorless crystals of the phenylxanthyl chloride separated. The material was crystallized several times, great care being taken to prevent hydrolysis. Any hydrogen chloride formed is not liberated but adds to unchanged material to form the highly colored chloride hydrochloride. Pure white, dry chloride turns bright yellow in a few seconds on exposure to air.

Crystallization from benzene involves one-half molecule of benzene of crystallization. The material used in runs one to seven was prepared from this solvent and melted at 86°.

Anal. Calcd. for $C_{19}H_{13}OCl\cdot{}^1/_2C_6H_6$: Cl, 10.70. Found: Cl, 10.60.

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[1] Kraus and Kahler, THIS JOURNAL, **55**, 3537 (1933), have associated the ease of oxidation of sodium triphenylmethyl with a small electron affinity. As the product of the reaction, however, is triphenylmethyl peroxide it would seem that the strength of the carbon oxygen bond is to be held responsible for much of this reactivity.

[2] Bent, THIS JOURNAL, **52**, 1498 (1930).

[3] Glockler, *Phys. Rev.*, **46**, 111 (1934).

[4] Mayer and Helmholz, *Z. Physik*, **75**, 19 (1932).

[5] Sutton and Mayer, *J. Chem. Phys.*, **3**, 20 (1935).

[6] Lederle, *Z. physik. Chem.*, **17B**, 362 (1932).

[7] Wheland, *J. Chem. Phys.*, **2**, 474 (1934), has come to the conclusion from a theoretical treatment of the resonance energy of free radicals that they should all have the same electron affinity.

[8] Gomberg and Cone, *Ann.*, **370**, 158 (1909).

The material used in runs eight to ten was recrystallized from petroleum ether. It melted at 104–105° (Gomberg gives 105°).

Anal. Calcd. for $C_{19}H_{13}OCl$: Cl, 12.12. Found: Cl, 12.25.

This material was also analyzed by hydrolyzing an ethereal solution with water and titrating with freshly prepared sodium carbonate solution, indicating a purity of 97%.

α-Naphthylxanthyl Chloride.—The preparation of the hydrol and the chloride was very similar to that described above.[9] The chloride was analyzed by titration. The rather slow hydrolysis of the last portion of the chloride probably accounts for a rather low result; m. p. 172–173° (Gomberg gives 172–173°).

Anal. Calcd. for $C_{23}H_{15}OCl$: Cl, 10.35. Found: Cl, 9.83, 10.04.

***p,p'*-Biphenylene-bi-(diphenylmethylcarbinol).**[10]—This dicarbinol was prepared according to the directions of Schlenk and Brauns[11] and the dichloride according to the directions of Chichibabin.[12] A crystalline powder was obtained melting at 222–223°, uncorr, (Chichibabin gives 219°). The chloride was analyzed by hydrolysis and titration and also by the Carius method. The latter only is given.

Anal. Calcd. for $C_{38}H_{28}Cl_2$: Cl, 12.78. Found: Cl, 12.34, 12.75.

The apparatus and procedure used in making the equilibrium measurements have been previously described. Results are given in Tables I and II.

TABLE I

EQUILIBRIUM DATA FOR THE REACTION OF ADDITION OF SODIUM TO SUBSTITUTED DIXANTHYL DERIVATIVES

Run	G. atoms Na removed × 10^4	G. atoms Na left × 10^4	Moles of ether	G. atoms of mercury	Log K_2 $K_1 = 10^{-2}$ $K_3 = 10^{-4}$	ΔF kcal.
			Diphenyldixanthyl			
1	1.71	0.421	0.334	1.695	12.13	
2	1.06	.53	.344	1.013	12.38	
3	1.355	.499	.338	2.405	12.54	
4	0.846	.354	.332	1.163	12.38	
5	1.292	.618	.338	0.700	12.16	
6	1.730	1.002	.388	0.585	12.11	
7	1.183	0.819	.328	1.028	12.57	
8	1.892	.738	.333	1.140	12.21	
9	0.511	.326	.291	0.583	12.46	
10	0.706	1.379	.274	0.128	12.38	
				Average	12.33	−16.9
			Di-α-naphthyldixanthyl			
					$K_1 = \infty$ $K_3 = 10^{-4}$	
1	0.788	0.397	0.324	0.708	12.17	
2	1.772	1.748	.390	.541	12.17	
3	0.859	0.753	.288	.344	12.18	
4	1.375	1.278	.353	.468	12.17	
5	0.467	0.411	.255	.249	12.24	
				Average	12.2	−16.7

TABLE II

EQUILIBRIUM DATA FOR THE REACTION OF ADDITION OF SODIUM TO FREE RADICALS IN SOLUTION IN BENZENE WITH 3% ETHER (BY VOLUME)

Run	G. atoms Na removed × 10^4	G. Atoms Na left × 10^4	Moles of ether	G. atoms of mercury	Log Log K_4	ΔF kcal.
			Triphenylmethyl			
1	1.482	0.058	0.31	0.0602	14.04	
2	3.363	.377	.775	.0135	13.15	
3	1.463	.507	.461	.0150	14.25	
4	1.315	.278	.367	.0153	14.12	
				Average	13.89	−18.9
			p,p'-Biphenylene-bi-(diphenylmethyl)			
1	0.876	0.127	0.36	1.16	16.17	
2	.346	.190	.44	0.49	16.78	
3	.167	.140	.67	.121	16.67	
4	.140	.090	1.264	.133	16.59	
				Average	16.55	−22.6

Considerable difficulty was encountered in finding a suitable solvent for *p,p'*-biphenylene-bi-(diphenylmethyl) and the sodium derivative. Ether could not be used on account of very small solubility. Pyridine cannot be used on account of its reactivity with 1% amalgam. Dioxane dissolves the chloride and the free radical but not the sodium derivative. In benzene no sodium derivative was formed. Finally a mixed solvent was used prepared by adding 3% of ether to benzene. The results are not as good as in the case of other compounds studied but are of sufficient accuracy to permit certain conclusions.

Discussion

If we represent a free radical by "R" the reaction of addition of sodium may be described by the equations

$$R_2 \longrightarrow 2R \qquad (1)$$

$$Na + R \longrightarrow Na^+ + R^- \qquad (2)$$

The values given for the free energy change of reaction (2) in the tables have been calculated by the method described in earlier papers of this series.[13] In these calculations we have assumed a value of 10^{-4} for the dissociation constant for reaction (3)

$$NaR \longrightarrow Na^+ + R^- \qquad (3)$$

An investigation soon to be reported from this Laboratory indicates that this value is much too large, but that complex ions are not important at the concentrations used in these experiments.[14]

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(9) Gomberg and Schoepfle, THIS JOURNAL, **39**, 1668 (1917).

(10) This preparation was conducted under the direction of Professor E. P. Kohler.

(11) Schlenk and Brauns, *Ber.*, **48**, 723 (1915).

(12) Chichibabin, *ibid.*, **40**, 1818 (1907).

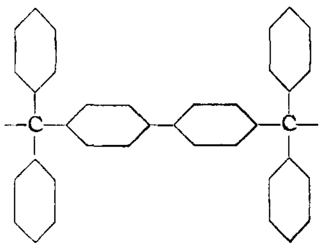
(13) Bent, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); Bent and Dorfman, *ibid.*, **54**, 1393 (1932); Bent, Dorfman and Bruce, *ibid.*, **54**, 3250 (1932).

(14) It would be possible to assume a value for K_3 very much smaller than 10^{-4} and much closer to the probable value for this constant. However, we hope to determine the value for this constant experimentally and it would therefore seem unwise to recalculate our previous data and the data given in this paper with such an assumed value only to repeat the process with the experimental value. The value 10^{-4} was based on very limited experimental data but was the best estimate we could make at the time of writing the first paper of this series.

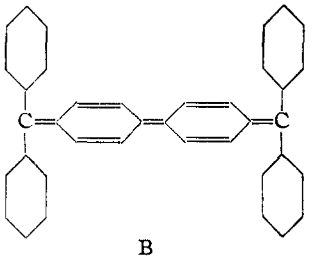
We are probably justified in assuming the dissociation constants of sodium addition compounds of various free radicals to be about the same. This follows from the discovery by Kraus and Fuoss[15] that the ionic size is the determining factor with a given solvent. The sodium ion is common to all of the salts which we have studied and therefore contributes a constant ionic size to the ionic distance "*a*" of Kraus and Fuoss. The negative free radical ion is changing in size to only a slight extent as we pass from one compound to another. Since we are interested in relative values of the free energy change for reaction (2) a change in the constant for reaction (3) will not affect our conclusions.

The values of 16.9 and 16.7 for the free energy change associated with the addition of sodium to the two free radicals of the xanthyl series are to be compared with values ranging from 17.9 to 20.6 for the various hydrocarbon free radicals previously studied. If we compare phenylxanthyl (16.9) with triphenylmethyl (17.9), we see that the introduction of an oxygen atom in the ortho position in two of the phenyl groups lowers the free energy by one kilogram calorie. The magnitude of this effect is so small as not to be very significant.

We consider next the very interesting compound *p,p'*-biphenylene-bi-(diphenylmethyl). This compound is interesting on account of the fact that it may be written either as a di-free radical (A) or as a quinonoid structure (B). Since it reacts rapidly with oxygen to give a colorless peroxide[16] it has been regarded as either completely in the form of the di-free radical or as an equilibrium mixture of the two forms.



A



B

It should be borne in mind, however, that the two structures are not isomers but represent different electronic configurations which together represent the molecule. One might expect that sodium would add with much less ease to this compound than to triphenylmethyl on account of the stabilizing effect of the quinonoid structure. The experimental results in Table II, however, indicate that sodium adds more readily to this substance than it does to triphenylmethyl. The values for K_4 (as used in the first paper of this series) refer to the reaction Na + R = NaR and not to the reaction leading to the formation of ions. Inasmuch as a different solvent had to be used for this compound, it seems better to consider this reaction until we have more information on the ionization constant of the sodium addition compound.

Part of the explanation of this reactivity toward sodium follows directly from a consideration of the resonance energy of the molecule and the values for single bond energies. Pauling and Wheland[17] have shown that it is possible to account for the dissociation of hexaphenylethane to triphenylmethyl by the large resonance energy of the latter. Similar considerations indicate that *p,p'*-biphenylene-bi-(diphenylmethyl) is to be considered almost entirely as in the free radical form. In the first place, the resonance energy is larger for this compound than for triphenylmethyl and in the second place the energy necessary to change a double bond to a single bond (pass from the quinonoid form to one free radical structure) is less than that required to break a single bond. This accounts for the quinonoid form contributing little to the stability of the free radical and hence only a small loss in stability in forming the sodium addition compound. The fact that sodium adds *more* readily than to triphenylmethyl suggests that the resonance energy of a pair of electrons is somewhat greater than for a single electron, assuming the same number of structures in both cases. This question apparently has not been answered by quantum mechanics at present.

The above discussion is clearer when applied to benzoquinone for which more data are available.

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(15) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933), and following papers.

(16) Chichibabin, *Ber.*, **40**, 1818 (1907).

(17) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

Benzoquinone may be written as either of two structures as in the case above

A

B

Pauling has recently calculated the resonance energy of quinone to be 0.23 e.v. and has suggested structure (A) to account for this stability. The addition of hydrogen to quinone is comparable to the addition of sodium to a di-free radical. We may consider the addition of hydrogen to take place according to the steps given below, the structures represented by (A) and (B) having only the stability expected for one electronic structure. The energies given for reactions (a) and (e) are then the resonance energies of these compounds.

	ΔH, e. v.	
Benzoquinone $\longrightarrow$ B	0.58	(a)
B $\longrightarrow$ A	5.51	(b)
$H_2 \longrightarrow 2H$	4.44	(c)
$A + 2H \longrightarrow AH_2$	−9.50	(d)
$AH_2 \longrightarrow$ Hydroquinone	−2.48	(e)
Total	−1.45	(f)

Reactions (a), (b), and (c) are written in order to assign processes corresponding to the values of ΔH calculated by considering the difference in the single bond energies for the reactants and products. It is interesting to note that if no resonance energy were involved the hydrogenation of quinone would be an endothermic reaction. The values given for the resonance energy in (d) and (e) are taken from Pauling's data and were calculated by him from thermal data. The final value (f) may be compared with that obtained experimentally by Conant[18] for the heat of hydrogenation in the vapor phase of 1.35 e. v. An alternative way of treating the data would be to consider the heat of hydrogenation known from the data of Conant and from combustion data. The cycle would then give an independent way of calculating the resonance energy of, say, hydroquinone, assuming all of the other factors to be known. In either case the agreement is very satisfactory. Equation (a) indicates that the free radical structure is much less stable than the quinone structure and therefore contributes relatively little to the stability of the molecule. Had one started by writing the free radical structure for quinone and calculated the resonance energy due to the quinonoid structure one would have obtained 6.1 e.v. for the resonance energy due to this structure. One may consider these two values (0.58 and 6.1) as indicating the relative importance of the free radical and quinonoid structures in the normal state of quinone. This conclusion is quite in harmony with the facts of organic chemistry in assigning the quinonoid structure to benzoquinone.

Summary

1. The electron affinity of phenylxanthyl and of α-naphthylxanthyl have been measured and found to differ little from the values for organic free radicals previously studied.

2. Sodium has been found to add more easily to *p,p'*-biphenylene-bi-(diphenylmethyl) than to triphenylmethyl. This fact is interpreted in terms of single bond energies and resonance energy.

CAMBRIDGE, MASS. RECEIVED MAY 2, 1935

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[18] Conant, THIS JOURNAL, **49**, 293 (1927).