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On the Theory of Free Radicals and Organo-Alkali Compounds

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The theory of the free radicals of Pauling and Wheland is applied to the electron affinities of the radicals. The results are compared with the measurements of Bent, and they indicate that the charging electron enters in resonance with the whole system of $[p]_h$ -electrons. The theory is generalized to unsaturated hydrocarbon radicals and it is shown that the formation of ionizable metal derivatives is due to the resonance between the charging electron and the $[p]_h$ -electrons. Some cases of anomalous reactions of organo-alkali compounds are also interpreted.

E. HÜCKEL¹ as well as L. Pauling and G. W. Wheland² have proved that one can explain the dissociation of hydrocarbons in free radicals by a stabilization of the radicals. Earlier it was supposed that the dissociation was due to a weakening of the central C-C linking. This stabilization is caused by the resonance between the unpaired binding electron and the characteristic $[p]_h$ -electrons* of the aromatic substituents. Using certain simplifications one can calculate the term-values according to the general methods and arrive at a satisfactory approximation to the experimental values of the heat and degree of dissociation.

As a further application of this theory it seems likely to try to explain some of the other characteristic properties of the triarylmethyl-complex. An inquiry into this question shows that it is impossible in this way to obtain a better understanding of the electron-affinities of such radicals.

In the quantum mechanical calculation of the e.a. of such a free radical one can imagine *a priori* two possible ways. One may suppose the problem solved for the free radical and then add the last electron in the same way as one does in the simplest cases. Or one can treat all electrons together, determining at first the term-value of the odd number of electrons which correspond to the free radical, and afterwards that of the even number corresponding to the negative ion,

and equate the e.a. to the difference between the terms.

An investigation shows that the first method necessitates the introduction of rather arbitrary assumptions. The second method is closely related to that of Pauling and Wheland.³ To obtain the coefficients of the exchange integrals these authors use a set of "canonical structures" containing one electron more than the free radical. Afterwards they omit the exchange integrals where the "phantom orbit" partakes of the exchange. In their other approximations they agree with Hückel. The question consists essentially in transferring in a reasonable way the approximations to the ionic problem. We must then remember that the "neighboring" electrons of the charging electron will not be the same ones in all structures, as we must suppose that the last one has the same initial wave function (with opposite spin) as the unpaired electron of the free radical. In a matrix element in the secular equation of the ion we therefore introduce the simple exchange integrals only where the charging electron is exchanged with its "partner" in the one or the other of the two structures of which the matrix element is formed. These will be "binding" exchange integrals. We shall suppose them to be equal to the other exchange integrals of neighboring electrons. This is only a rather rough approximation because the excess negative charge will probably weaken somewhat the exchange effect. On the other hand we thereby avoid the introducing of new

¹ Hückel, *Zeits. f. Physik* **83**, 632 (1933).

² Wheland, *J. Chem. Phys.* **1**, 362 (1933).

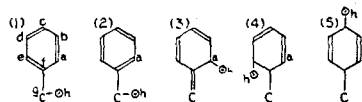
* Designation of Hückel. It means the electrons that cannot be placed in ordinary single bonds of an aromatic nucleus or of a double bond. H. supposes them to have wave functions with a node in the plane of the ring.

³ See further: J. C. Slater, *Phys. Rev.* **38**, 1109 (1931); G. Rumer, *Nachr. d. k. Ges. d. Wiss. zu Göttingen M. P. Klasse*, p. 337 (1932); Pauling, *J. Chem. Phys.* **1**, 280 (1933).

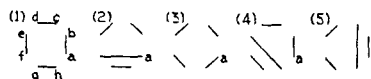
parameters which must be determined by the empirical data. In addition we make the strongly approximate assumption that the "non-binding" exchange integrals of the "charging" electron are negligible. At last we suppose the Coulombian integrals of the radical and of the ion to be equal.

As can easily be seen, all these approximations affect the result in the direction of lower term-value of the ion, and we must therefore expect the electron affinity obtained to be too large.

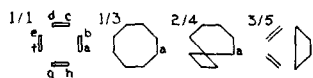
By the setting up and solving of the secular equation we proceed in the manner of Pauling and Wheland. To illustrate the method, we shall regard the case of the benzyl ion. Considering the following canonical structures:



with the corresponding schemes:



we get e.g. the following schemes of the matrix elements:



which give:

$$\begin{aligned} H_{1,1} &= Q + ab + cd + ef + gh - 1/2af - 1/2bc - 1/2de - 1/2fg = Q + 2\alpha \\ H_{1,3} &= 1/8Q + 1/8(ab + af + bc + cd + de + ef + fg + ah + gh) = 1/8Q + 9/8\alpha \\ H_{3,4} &= 1/8Q + 1/8(ab + af + bc + cd + de + ef + fg + eh + gh) = 1/8Q + 9/8\alpha \\ H_{3,5} &= 1/2Q + 1/2(ab - 1/2af + bc - 1/2cd + de - 1/2ef + fg + ah + ch) = 1/2Q + 9/4\alpha \end{aligned}$$

where Q is the Coulombian integral and α the simple exchange integral. The secular equation will then be:

$$\begin{vmatrix} (Q-W)+2\alpha & 1/4(Q-W)+13/8\alpha & 1/8(Q-W)+9/8\alpha & 1/2(Q-W)+9/4\alpha & 1/4(Q-W)+3/2\alpha \\ 1/4(Q-W)+13/8\alpha & (Q-W)+2\alpha & 1/2(Q-W)+9/4\alpha & 1/8(Q-W)+9/8\alpha & 1/4(Q-W)+3/2\alpha \\ 1/8(Q-W)+9/8\alpha & 1/2(Q-W)+9/4\alpha & (Q-W)+2\alpha & 1/4(Q-W)+3/2\alpha & 1/2(Q-W)+9/4\alpha \\ 1/2(Q-W)+9/4\alpha & 1/8(Q-W)+9/8\alpha & 1/4(Q-W)+3/2\alpha & (Q-W)+2\alpha & 1/2(Q-W)+9/4\alpha \\ 1/4(Q-W)+3/2\alpha & 1/4(Q-W)+3/2\alpha & 1/2(Q-W)+9/4\alpha & 1/2(Q-W)+9/4\alpha & (Q-W)+2\alpha \end{vmatrix} = 0.$$

Supposing that the structures 1 and 2 as well as 3, 4 and 5 enter into the linear combination with the same coefficients, the equation will be reduced to:

$$\begin{vmatrix} 5/2(Q-W)+29/4\alpha & 7/4(Q-W)+39/4\alpha \\ 7/4(Q-W)+39/4\alpha & 11/2(Q-W)+18\alpha \end{vmatrix} = 0.$$

Hence

$$W = Q + 3.8979\alpha,$$

and with

$$W' = Q + 2.4091\alpha,$$

the e.a. will be

$$\Delta W = W' - W = +1.4887\alpha.$$

According to Pauling and Wheland we can obtain the coefficients of the Coulombian and exchange integrals in a matrix element of the reduced secular equation of a composed radical by means of the formulae:

$$\begin{aligned} \sum q &= \sum q_1 \sum q_2 \sum q_3, \\ \sum a &= \sum a_1 \sum q_2 \sum q_3 + \sum q_1 \sum a_2 \sum q_3 + \sum q_1 \sum q_2 \sum a_3, \end{aligned}$$

where $\sum q_i$ is the coefficient of the Coulombian and $\sum a_i$ that of the exchange integral in the reduced secular equation of the simple radical $R_{(i)}-CH_2$. These rules can be used in the ionic problem too. We then get e.g. the reduced equation of the triphenylmethyl ion:

$$\begin{vmatrix} 125/8(Q-W)+2175/16\alpha & 343/64(Q-W)+5733/64\alpha \\ 343/64(Q-W)+5733/64\alpha & 1331/8(Q-W)+6531/4\alpha \end{vmatrix} = 0,$$

$$W = Q + 10.1445\alpha, \quad \Delta W = -3.3362\alpha.$$

TABLE I.

		-W	V.e.	KgC.	V.e.
Benzyl	$C_6H_5CH_2-$	1.489	2.08		
α -naphthylmethyl	$\alpha-C_{10}H_7CH_2-$	1.565	2.19		
β -naphthylmethyl	$\beta-C_{10}H_7CH_2-$	1.549	2.17		
Biphenylmethyl	$C_{12}H_9CH_2-$	1.564	2.18		
Diphenylmethyl	$(C_6H_5)_2CH-$	2.498	3.50		
Triphenylmethyl	$(C_6H_5)_3C-$	3.336	4.67	17.9	2.55 \pm 0.22
Diphenyl- α -naphthylmethyl	$(C_6H_5)_2(\alpha-C_{10}H_7)C-$	4.299	6.02	18.6	
Diphenyl-biphenylmethyl	$(C_6H_5)_2(C_{12}H_9)C-$	4.271	5.98	19.1	
Phenyl- α -naphthyl-biphenylmethyl	$(C_6H_5)(\alpha-C_{10}H_7)(C_{12}H_9)C-$	4.493	6.30	19.5	
Phenyl-diphenylmethyl	$(C_6H_5)(C_6H_5)_2C-$	4.430	6.20	19.8	
Tri-biphenylmethyl	$(C_{12}H_9)_3C-$	4.687	6.56	20.6	
α -naphthyl-diphenylmethyl	$(\alpha-C_{10}H_7)(C_6H_5)_2C-$	4.679	6.55	20.2	
Diphenyl- β -naphthylmethyl	$(C_6H_5)_2(\beta-C_{10}H_7)C-$	3.932	5.50	18.6	

Treating in the same way α -naphthyl; β -naphthyl and biphenyl substituted methyl groups we find the values which are given in Table I. In the second column we have quoted the values of the e.a. putting $\alpha=1.4$ v.e. In the third column are given the e.a.'s measured by Bent and co-workers⁴ for an ether solution; in the fourth the result for triphenylmethyl for the gaseous state. Bent has only calculated this value for the gaseous state, but accepting his own considerations the two values will provide a good basis for comparison.

We first note that the value for triphenylmethyl is too high, which is in agreement with our prediction. The difference, however, appears to be larger than might have been expected, since our calculations concern the normal state i.e., the absolute zero, while the measurements of Bent were carried out at a temperature $T=298^\circ K$. For the other radicals the differences ought—according to the opinion of Bent—to be somewhat greater for the gaseous state than for the ether solution, in agreement with our theoretical expectations. It seems, however, as if the values for the radicals containing the α -naphthyl group turn somewhat out of the course of the empirical data, a circumstance for which we cannot give any plausible explanation, though it might perhaps be corrected by a slight improvement of the calculation method. It might in this connection be recalled that the α -naphthyl group shows a stronger dissociating

influence upon hexa-aryl substituted ethanes than the β -naphthyl group.⁵

Whatever may be added to this point, the explanation of the relatively pronounced electron affinity of the free radicals (and of other special hydrocarbon-radicals (see below)) seems to lie in the fact that *the charging electron enters in resonance with the whole system of $[p]_k$ -electrons.*

However, not only the free radicals but a good many other hydrocarbon-radicals are known to give alkali compounds of a similar character. All of these are characterized by unsaturation. We shall see that many of the affiliated questions obtain a reasonable solution when we consider them from our point of view. Some of these problems are already touched upon by Hückel⁶ though he has not undertaken a more systematic investigation of the experimental material.⁷

We shall concentrate on types of compounds which are in the line with the free radicals, i.e., where the marked e.a. apparently is bound to certain carbon atoms substituted with unsaturated groups. This corresponds to the "reactive" or "acid methylene" of classical chemistry. Using this point of view we find that the predominant part of the phenomena—as can easily be seen—is attached to the methylene (or for three substituents methenyl-) groups of this sort.

By the method used here, one can first easily

⁵ P. Walden, *Chemie der freien Radikale*, p. 296, Lpz. 1924.

⁶ Zeits. f. Physik 70, 204 (1931); 76, 628 (1932).

⁷ See the summaries of Wooster, Chem. Rev. 11, 1 (1932); Schmidt, *Organometallverbindungen II*, Stuttgart. 1934.

⁴ H. E. Bent, J. Am. Chem. Soc. 52, 1498 (1930); 53, 1780 (1931). Bent and M. Dorfman, J. Am. Chem. Soc. 54, 1393 (1932).

calculate the e.a. of a radical of the type $R-CH=CH-CH_2$ by supposing resonance between the structures:

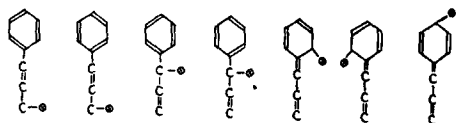


We then get the e.a.

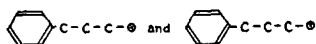
$$W=1,333\alpha.$$

For unsaturated radicals with a triple bond the problem is a good deal more complicated, as we do not know the electronic structure of such a bond. There is, however, every reason to suppose that at least one pair of the electrons of the bond is formed by $[p]_k$ -electrons and can enter into resonance with the charging electron. Probably also a second one of the electron pairs is formed in a similar way and contributes to the resonance. The stronger electronegative effect⁸ seems to support this assumption. The electronic structure of the triple carbon-carbon bond has, however, claim to a separate and broader investigation, as it has a good deal of chemical interest because of the peculiar metal compounds of the type $R-C\equiv C-Me^1$.

It is further—still under the point of view of the "acid methylene"—of interest to point out that the transmission of the effect of an aromatic nucleus through a double bond² is easily explained when we consider the possible structures of such a radical in comparison with the corresponding unsaturated radical. We can, e.g., for the cinnamyl-radical expect resonance between the following structures:



while the corresponding hydrocinnamyl-radical only permits resonance between:



We can now make similar considerations concerning more complicated substituents and show that similar circumstances must exist—not

only in case of the previously treated aromatic nuclei—but also in case of longer chains of *conjugated* double bonds etc.

It might have been of interest to consider some more of the material concerning organo-alkali compounds from the point of view of "acid methylene," because some of those who have been occupied with the subject seem to have overlooked the close analogy between the aryl- and unsaturated- substituted "acid methylene" (and methenyl). By going over the material³ one can, however, convince oneself of the role played by the aromatic and unsaturated substituents by the easy forming of alkali derivatives. One can further without difficulty see that the reactions have a pronounced tendency to be connected with just those carbon atoms which are substituted with such groups. We may then be content by establishing the following conclusion: With the exception of the acetylenides, *a smooth substitution or addition of alkali metal to a hydrocarbon with the forming of an easily ionizable (generally strongly colored) alkali compound will take place only at such places in the molecule where the embodied charging electron (s) can enter into resonance with the $[p]_k$ -electrons of aromatic or unsaturated substituents.*

Hereby nothing is, of course, said about the places in the molecule where the reactions of the formed ion are connected; nor anything whether a substitution or an addition will be the reaction really taking place.

We have not yet touched the interesting question whether the supposed resonance between the different localizations of the charging electron has any direct chemical meaning. To examine this we recall the case of the benzyl ion. In that case—as in the other ones—we supposed the different structures (five) to be in resonance, and searched for the "right" linear combination $\psi = \sum c_i \psi_i$ of the wave functions ψ_i of the initial states. We found this by introducing the electron interaction and solving the corresponding secular equation. In the language of the statistical interpretation this means that there is some probability to find the charging electron at the ortho- and para-position in the nucleus. Supposing as before, the structures to be orthogonal and the ψ_i 's normalized, we find in this case:

⁸ L. Lapayre, Thèse, Lyon 1930.

⁹ G. Wittig and M. Leo, Ber. 63, 943 (1930); E. Bergmann, Ber. 63, 2593 (1930); Wittig, Ber. 64, 477 (1931); see also reference 8.

$$\psi = 0.20188(\psi_1 + \psi_2) + 0.1580(\psi_3 + \psi_4 + \psi_5).$$

The probability is then a finite one. We hence draw the conclusion, without making any assumption of the mechanism of the reactions, that one can expect some of the reactions of the ion to be connected with the para- and ortho-position.

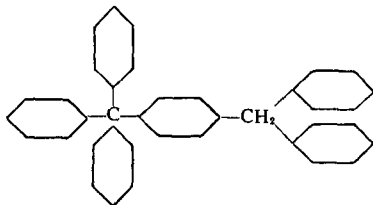
We shall see that this conclusion is confirmed by certain—though few—anomalous reactions of the alkali compounds of benzyl and similar compounds. As a case of ortho-reaction may be mentioned that benzyl-sodium and-lithium with formaldehyde gives orthotolylalcohol.¹⁰ The same product is obtained by treating benzylmagnesium-chloride with trioxymethylene. A para-reaction is, as far as we know, never found in the case of benzyl; the reaction of triphenylmethyl-sodium with triphenylacetyl-chloride, however, which gives *p*-benzhydryl- ω,ω',ω'' -triphenyl-acetophenone¹¹ is an example of such a reaction. In the same connection may be mentioned the polymerization of triphenylmethyl to *p*-benzhydryl-tetraphenylmethane with sodium as a catalyst.¹² That this reaction takes place with hydrogen chloride and even autocatalytically should not surprise us, as we ought to expect similar conditions in the case of the free radicals. A similar—though not so clear—case with an unsaturated radical we meet in cinnamylmagnesium-chloride which apparently reacts as $\text{C}_6\text{H}_5\text{C}(\text{MgCl})=\text{CH}-\text{CH}_3$.¹³ We must here suppose a secondary displacement of the double bond. The $\Delta^{\alpha,\beta}$ -compound should be preferred from considerations of energy, on account of the conjugation of the double bond with the aromatic nucleus.

¹⁰ Wooster, reference 7, p. 18, 32.

¹¹ Wooster, reference 7, p. 33.

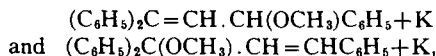
¹² Walden, reference 5, p. 80 note.

The formula of *p*-benzhydryl-tetraphenylmethane is



¹³ Gilman and Harris, J. Am. Chem. Soc. 53, 3541 (1931).

An especially illuminating case of an anomalous reaction we find in the reactions



which give identical metal compounds (yielding identical products by all chemical reactions). The same holds for the corresponding hydrocarbons (with H for OCH_3) by the action of phenylisopropyl-potassium.¹⁴

It will be shown by these few examples that the supposed resonance so far from contradicting the chemical facts, rather completes and explains them in a quite satisfactory manner.

Before finishing our considerations, we may mention a case which seems to fall somewhat outside the theory outlined here. The addition products of stilbene with lithium and sodium¹⁵ yield by action of carbon dioxide, meso- *viz.* racemic diphenyl-succinic acid, a phenomenon which seems to be difficult to reconcile with the supposed resonance. It is however as Ch. B. Wooster¹⁶ has pointed out, by no means excluded that there exists stereoisomerism between the ions formed. In our opinion the different color of the two addition products makes an assumption of different electronic structure obvious. At any rate there does not seem to be any reason to expect that a more thorough discussion of this exceptional case will entail any considerable revision of the theory outlined above.

An obvious further task of the above theory of free radicals is the interpretation of the positive "carbonium" ions. This problem seems to offer rather great difficulties. For the first, it seems as if the binding of the unpaired electron were entirely Coulombic in nature as, e.g., the benzyl radical only exceeds the positive benzylium ion with a minimum (0.0091α) resonance energy. Second, the substituents in the aromatic nuclei play a rather great role for the formation of a base, a fact that will complicate the quantum mechanical treatment a good deal. Nevertheless the task is enticing, inasmuch as one possibly could throw some light on the many interesting phenomena which are connected with the great and important group of triphenylmethane dyes.

¹⁴ Wooster, reference 7, p. 55f.

¹⁵ Wooster, reference 7, p. 27.

¹⁶ Wooster, reference 7, p. 27f.