

157°) predominating. The molal ratio of total chlorine reacting to ethylene reacting varies from two to eleven in the present experiments, and is greater the lower the partial pressure of ethylene. This is explained on the basis of chain mechanisms for both the ethylene-chlorine and benzene-chlorine reactions, the latter being induced by and acting as an inhibitor of the former.

In homogeneous solution the above ratio, with chlorine in large excess, is approximately two. A higher proportion of the chlorine is used in substitution than in the heterogeneous reactions.

No evidence of a Friedel-Crafts type of reaction between the ethylene chloride formed and benzene could be found. In a mixture of benzene, benzoyl chloride and chlorine no benzophenone was formed with introduction of ethylene.

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THE REDUCTION POTENTIALS OF SOME HIGHER BENZOLOGUES OF THE QUINONES

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With the view of applying certain new tests to the theories of the structure of anthracene, we have prepared three angular dibenz-anthraquinones,¹ and determined their reduction potentials. It seemed appropriate to include in this study other quinones derived from tetra- or pentacyclic hydrocarbons, and we have thus examined potentiometrically most of the known compounds of this type.

We were fortunate in securing a sample of picenequinone through the kindness of Professor Frederick D. Chattaway of Oxford University, while the chrysene used in the preparation of the 5,6-quinone was furnished by the Gesellschaft für Teerverwertung through the courtesy of the late Dr. R. Weissgerber. The other derivatives of 5,6-chrysenequinone, as well as the 6,12-isomer, were prepared by the synthesis of Beschke and Diehm.²

The results of the electrometric titrations are summarized in the accompanying table. The nature of the titrating reagent indicates the method of titration employed; in most cases it was found expedient to reduce the quinone catalytically and to titrate the reductant with an oxidizing agent. While satisfactory results were easily obtained with the tetracyclic quinones, the very sparing solubility of the pentacyclic compounds presented a serious obstacle. With the very dilute solutions slight sources of error have a magnified effect upon the potentials. It

¹ Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

² Beschke and Diehm, *Ann.*, **384**, 143 (1911).

TABLE I
 REDUCTION POTENTIALS AT 25°

Quinone	Solvent: 95% alcohol, 0.2 N in HCl and 0.2 N in LiCl		Normal potential E_0 , v.				ΔE_1 , mv.	ΔE_2 , mv.	E_0 (av.), v.
	Molality of quinone	Titrating agent ^a							
1,2-Benzanthra-	0.0003	A	0.228	0.228	0.229		18.7	20.9	0.228
1,2,7,8-Dibenzan-									
thra-	.00006	B	.266	.264	.262		18.3	17.3	.26±
1,2,5,6-Dibenzan-									
thra-	.00013	A	.270	.265	.268		19.0	26.3	.268
(1,2)-Bz-3-metho-									
1,2,5,6-dibenz-									
anthra-	.00015	A	.258	.259	.255		17.8	20.2	.257
5,6-Chrysene-	.0004	A,B	.465	.464	.466	0.464	18.9	19.1	.465
6,12-Chrysene-	.0001	B	.391	.393	.392	.393	17.9	17.9	.392
12-Hydroxy-5,6-									
chrysene-	.0001	B	.392	.391	.391		17.3	18.2	.391
12-Ethoxy-5,6-									
chrysene-	.0001	B	.418	.418	.419	.418	19.5	21.1	.418
1,2-Benz-3,4-an-									
thra- ³	.0001	C	.433	.428	.430	.430	18.6	20.2	.430
Picene-	.00006	B	.463	.477	.486	.470	57.0	71.0	.474±0.01

^a Titrating agents: A, *p*-benzoquinone; B, tetrabromo-*o*-benzoquinone; C, 0.3 cc. of titanous chloride (20% solution) diluted to 50 cc. with the solvent.

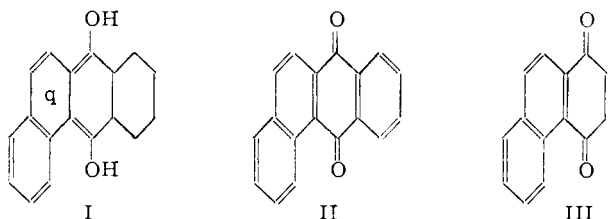
was further found that electrode equilibrium was established very slowly in the titrations with these compounds; a steady value sometimes was reached only after a period of one hour. The consequent errors are reflected in the divergence of the separate determinations of the normal potential, E_0 , particularly in the case of picenequinone. Because of the added uncertainty indicated by the wide deviation of the slope of the titration curve (ΔE_1 and ΔE_2) from the theoretical value ($\Delta E = 17.8$ mv.), the potential found for this compound is regarded as only an approximation.

The Structure of Anthracene.—It has been pointed out⁴ that the abnormally low reduction potential of anthraquinone may be interpreted as an indication of the unusual reactivity of the anthracene nucleus. According to current theories, the seat of this reactivity may be either an ortho-quinonoid grouping of the double bonds or a para bond between the meso carbon atoms. While it is not easy to predicate the implications of the para-bond theory, for such a structure is purely hypothetical, the ortho-quinones are well-known substances and rational predictions of the properties of the benzologues of anthracene can be constructed from the assumption of the ortho-quinonoid structure of the hydrocarbon.

On the basis of this theory the attachment to anthrahydroquinone of a phenylene group in the angular position, as in I, should stabilize the

³ Fieser and Dietz, *THIS JOURNAL*, 51, 3141 (1929).

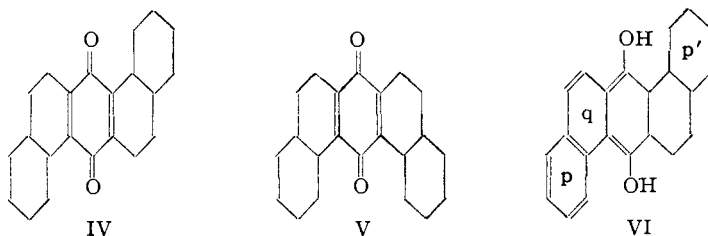
⁴ Fieser and Ames, *ibid.*, 49, 2611 (1927).



compound, in the sense of decreasing its tendency to undergo oxidation and thus relieve the tension in the ortho-quinonoid nucleus (q). This follows from the fact that β -naphthoquinone is more stable, in the same sense, than *o*-benzoquinone. This stabilizing effect of the added phenylene group would be expected to result in an increase in the oxidation-reduction potential of the system of which 1,2-benz-anthrahydroquinone is the reductant. The question of the possible influence of the extra benzene ring present in the oxidant, II, on the nature of the anthraquinone molecule can be readily answered by comparing 1,4-phenanthrenequinone, III, and 1,4-naphthoquinone. The latter compounds differ in just the way that 1,2-benz-anthraquinone differs from anthraquinone; a quinonoid ethylene linkage is in one case a part of a naphthalene ring, in the other case it is incorporated in a benzene nucleus. The potential of the naphthalene-containing compound, III, is the higher by 40 mv.⁵

If the extra phenylene group had no influence on the character of the reductant in question, the potential of the system from 1,2-benzanthraquinone would be expected to be 40 mv. higher than that from anthraquinone ($E_0 = 0.155$ v.),⁶ or 0.195 v. The actual potential is 0.228 v., 73 mv. above that of the parent compound. It is reasonable to attribute the extra increment to the stabilizing of the *o*-quinonoid system of the reductant, in the manner indicated.

In the case of the dibenz-anthraquinones, IV and V, the second angular phenylene may be expected to have the same influence on the nature of the oxidant as the first such group, and this would give an increase in the potential of 40 mv. over that of 1,2-benzanthraquinone. Examination



⁵ Fieser, *THIS JOURNAL*, 51, 3101 (1929). The difference in the potentials is erroneously reported in Table II of this paper as amounting to 30 mv.

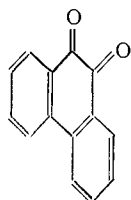
⁶ Conant and Fieser, *ibid.*, 46, 1858 (1924).

of the *o*-quinonoid formula for one of the reductants, such as VI, reveals the fact that while the first phenylene group, *p*, is in a position to stabilize the quinonoid structure in the anthracene nucleus, the second group, *p'*, cannot be attached at the same time to the quinonoid ring and therefore cannot influence its reactivity. According to the theory, then, the angular dibenz-anthraquinones should differ in potential from the monobenz-derivatives by approximately 40 mv., and not by the larger figure of 73 mv. which represents the effect of a single phenylene group. The results given in the table show that the difference for the two quinones, IV and V, amounts to 36 mv. and 40 mv., respectively, and the good agreement with the predictions based upon the *o*-quinonoid theory of the structure of anthracene constitutes an argument in support of this theory.

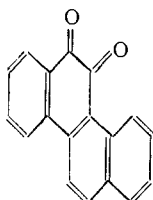
While the *p*-bond theory leads to no precise predictions of the effect of attaching an angular phenylene group to anthracene, it does imply that a second such group would have exactly the same influence as the first, for the *p*-bond formula is symmetrical. The present results show, however, that this is not the case and that, contrary to the *p*-bond theory, anthracene appears to have an unsymmetrical structure. It is unfortunate that the potential differences upon which these arguments are based are not more pronounced. The above conclusions appear justified, but they lack the weight to which they might otherwise lay claim.

The linear benz- and dibenz-anthraquinones offer an interesting field for a continuation of the present study, but it was found that these compounds, for reasons which will be apparent from a forthcoming publication, are not amenable to potentiometric study.

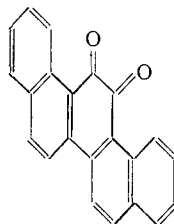
Benzologues of 9,10-Phenanthrenequinone.—5,6-Chrysenequinone, VIII, and picenequinone, IX, do not differ appreciably in potential from phenanthrenequinone, VII. While it is surprising that the added phenyl-



$E_0 = 0.471$ v.
VII



$E_0 = 0.465$ v.
VIII



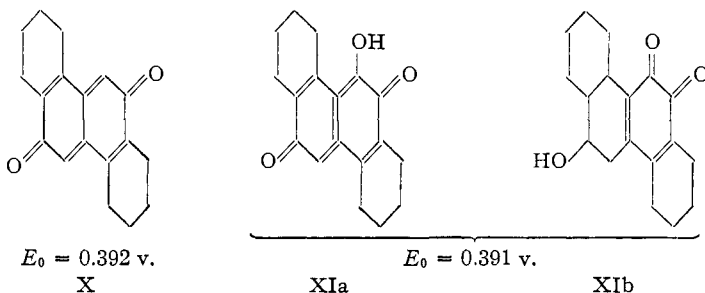
$E_0 = 0.474$ v.
IX

ene groups appear to have no influence, an adequate interpretation of the relationship will only be possible when the potential of the parent compound is more fully understood.

Amphi-chrysenequinone.—It is of interest to compare this substance, X, with amphi-naphthoquinone. The reduction potential of the latter

compound has been estimated by an indirect method to be 0.758 mv.⁷ By the inclusion of two of the quinonoid linkages of this substance in benzene rings the molecule is greatly stabilized and the potential is decreased by 0.366 v., or 0.183 v. for each such ring. This appears to be fairly consistent with the fact that the potential of *p*-benzoquinone is lowered 0.224 v. by the attachment to it of one phenylene group.

Hydroxy-chrysenequinone may conceivably exist in two tautomeric forms, XIa and XIb. Beschke and Diehm² have advanced chemical evidence in support of the ortho-quinonoid structure, XIb, and the electrochemical evidence confirms this view. If the structure of the compound



were that of an amphi-quinone, the potential should be in the neighborhood of 0.120 v. below that of amphi-chrysenequinone (effect of a quinonoid hydroxyl), that is, about 0.272 v. Since this differs from the actual value by over 0.1 v. it is obvious that the amphi-quinonoid structure is excluded. If, on the other hand, the compound has the structure of XIb, it would be expected to differ in potential from ortho-chrysenequinone to about the same extent that 3-hydroxy-phenanthrenequinone differs from the unsubstituted quinone, or 0.053 v. The potential predicted on this basis is $0.465 - 0.053 = 0.412 \text{ v.}$, and the figure is in fairly good agreement with the actual value of 0.391 v. The ortho-quinonoid formula is further supported by the fact that the ether, which is assuredly ortho-quinonoid, is just 0.027 v. higher in potential than the hydroxy compound. Such a relationship is entirely normal.

While the structure of hydroxy-amphi-chrysenequinone is thus established beyond question, the potential of this substance presents a striking anomaly. When Beschke and Diehm prepared the compound for the first time, they advanced the view that the substance must exist in that tautomeric form which has the lower reduction potential. This general principle has been elaborated and applied in a number of instances by one of us,⁸ and the generalization invariably has been confirmed. Beschke and Diehm had no means of estimating adequately the relative potentials

⁷ Fieser, *THIS JOURNAL*, 52, 5204 (1930).

⁸ Fieser, *ibid.*, 50, 439 (1928).

of the two tautomeric forms, but it is now clear that they were in error in considering that the ortho-quinonoid form would have the lower potential. The present results show that the stable tautomer is the one having the higher reduction potential, and the case thus constitutes a definite exception to the rule. The only suggestion which we can now offer in explanation of the failure of the hydroxyquinone to change over into a thermodynamically more stable tautomer is that there is some steric resistance to such a change.

Summary

A potentiometric study of the benzologues of anthraquinone and phenanthrenequinone has led to the following significant conclusions. (1) The potentials of the benz- and dibenz-anthraquinones lend support to the ortho-quinonoid theory of the structure of anthracene. (2) Hydroxy-chrysenequinone constitutes an exception to the rule that when a quinone can exist in two forms the one of lower potential will predominate.

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THE OXIMES OF ALPHA, BETA-UNSATURATED KETONES AND THE BECKMANN REARRANGEMENT

BY A. H. BLATT

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The work of Meisenheimer and others has brought into question the long-accepted assumption that in the Beckmann rearrangement a shift occurs between the oximino hydroxyl group and the hydrocarbon residue spatially adjacent—a *cis* migration—and has given new prominence to the view that the shift is between groups spatially removed—a *trans* migration. The original evidence to this effect was furnished by the ring opening of triphenyl isoxazole,¹ the bulk of the evidence, however, has come from the study of ring closure in appropriately substituted ketoximes.²

Although the chief evidence for the idea of a *trans* migration has come from the study of ring closure, there is one class of ketoximes, the oximes of α,β -unsaturated ketones, whose behavior seems incompatible with a *trans* migration.³

¹ Meisenheimer, *Ber.*, **54**, 3206 (1921).

² Meisenheimer and Meis, *ibid.*, **57**, 289 (1924); v. Auwers and Jordan, *ibid.*, **57**, 800 (1924); Brady and Bishop, *J. Chem. Soc.*, 127, 1357 (1925); Meisenheimer, Zimmermann and Kummer, *Ann.*, **446**, 208 (1926).

³ Von Auwers has discussed these oximes in a preliminary notice [*Ber.*, **62**, 1320 (1929)] and has outlined a series of researches on the oxime configurations and the relation between configuration, substituents and ease of ring closure. The present work was outlined and started several years ago. It was completed recently without knowl-