TABLE I

Compound	Wt., g.	Nitrogen, g.	% of total N in catholyte
Arginine	0.555	0.179	1.48
Asparagine	26.50	4.945	40.97
Betaine	4.46	0.533	4.42
Total	31.515	5.657	46.87

excess of cupric carbonate and filtered. The soluble fraction containing principally inorganic cupric salts was discarded. The insoluble residue on the filter was freed of copper with hydrogen sulfide and the aqueous solution concentrated by evaporation. On standing at 8-10° the nearly colorless solution yielded finally 4.91 g. of rhombic crystals which reduced potassium permanganate readily and melted at 190°. Characterization as oxalic acid was completed when the substance reacted with an excess of aniline to form oxanilide, m. p. 253°.

Discussion

Although the number of nitrogenous compounds isolated in this study was small, a high percentage of the nitrogen in certain fractions was accounted for as definite, crystalline substances, and nearly half of the total amount of catholyte nitrogen was similarly identified. Asparagine, for example, comprised 83% of the amide and 90% of the α-amino nitrogen found to be present. If the α-amino nitrogen of arginine is added to that of asparagine, the latter value is increased to 92%. Therefore the data show that the remaining amounts of these two forms of nitrogen as possible unidentified compounds do not exceed 0.2 g., respectively.

The possibility of the coexistence of the homolog of asparagine, glutamine, was realized but indicative tests for this common plant constituent were negative. However, another related compound, aspartic acid, was present in an amount too small for consideration and was of doubtful origin. Its presence may have been due to the hydrolysis of a small amount of asparagine during the isolation of the latter compound.

Identification of substances in the two basic nitrogen fractions (A, basic nitrogen in mercuric acetate precipitate, and B, basic nitrogen in filtrate from mercuric acetate precipitation) was less successful. Arginine, the only isolate from (A), comprised less than 20% of the nitrogen known to be present. In the (B) fraction the isolation of betaine identified more than half of the total amount of nitrogen indicated. Choline, a closely related plant constituent, if present, occurred in an amount too small for positive identification.

The "other nitrogen," segregated from the various nitrogenous groupings in the catholyte, constituted a substantial part of the total nitrogen but little or no knowledge of its composition was obtained in this study.

According to the isolation data asparagine and betaine were present to the extent of 2.65 and 0.45%, respectively, of the oven-dry weight of root bark. These concentrations appear sufficiently large to suggest that they may have some bearing on the chemistry and physiology of nitrogen reserves in the cotton plant. One may conjecture that part of the nitrogen accumulating at plant maturity is stored in the root bark in the form of these compounds.

Summary

Arginine, asparagine, betaine and oxalic acid were isolated in significant quantities from the electrodialyzates of extracts from cotton root bark.

Approximately half of the total organic nitrogen content of the catholyte was accounted for as definite compounds of which asparagine was predominant.

COLLEGE STATION, TEXAS RECEIVED OCTOBER 15, 1945

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

A Relation between the Oxidation-Reduction Potentials of Quinones and the Resonance Energies of Quinones and of Hydroquinones

BY ERNST BERLINER

The normal oxidation-reduction potential of a quinone is a measure of the free energy of reduction by hydrogen of the quinone to the hydroquinone, and expresses the oxidizing power of the quinone with reference to that of hydrogen ions. Measurements of potentials of many quinones have shown that substitution in the quinone changes the potential in a manner fairly well predictable by means of resonance or inductive effects of the substituent group.[1,2] Also, fusion of one or more benzene rings to the quinone ring invariably lowers the potential.

The main structural difference between a quinone and the corresponding hydroquinone is the cyclic unsaturated ketonic structure in the quinone and the aromatic ring in the hydroquinone. Although both compounds are stabilized by a certain amount of resonance energy, the stabilizing energy inherent in the aromatic ring system certainly outweighs the amount of resonance energy possessed by the quinone. Since almost all quinones have a positive potential, *i. e.*, they are reducible by hydrogen on a platinum electrode, the assumption is reasonable that the driv-

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(1) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 315.

(2) Fieser and Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1944, p. 729.

ing force for the reduction is the resonance energy gained by reduction to the hydroquinone. Since the ease of reduction of the quinone to the hydroquinone is expressed by the potential, a relationship should exist between the difference in resonance energies of the quinone–hydroquinone system and the potential.

That such a relationship exists was first demonstrated by Branch and Calvin (ref. 1, p. 304–314). These authors counted the number of contributing forms in the quinone and in the hydroquinone (one form in benzoquinone, two in hydroquinone), and obtained a straight line on plotting the ratio of the number of contributing forms against the potential. A still better relationship was obtained when the expression $\frac{n_H - n_Q}{n_H + n_Q}$ was used instead of the simple ratio and when allowance was made for steric and *ortho* effects in quinones of polynuclear structure. Ionic contributions from the oxygenated functions were omitted, because the authors assumed that these would be identical for all cases and therefore would be cancelled. The excellent relationship that was obtained justifies these assumptions. In the calculations by Branch and Calvin quinones of widely different ring systems were considered; but quinones having simple substituents, such as chloro or alkyl groups, which show distinctly different potentials, could not be included, owing to the nature of the method used.

In the present investigation a survey of the literature was made and data were collected from which the so-called empirical resonance energies of a number of quinones and the respective hydroquinones were computed. The difference between the resonance energies of the quinone and the hydroquinone was compared with the potential. Most of the figures were obtained from heats of combustion, from which the resonance energies were calculated by means of Pauling's values for the bond energies and the formulas given by Wheland.[3,4] A comparison of electrochemical with thermochemical values suffers from the limitation that potentials can be measured with a high degree of accuracy, whereas resonance energies, obtained from heats of combustion, are less exact, which is mainly a result of experimental errors in carrying out determinations of heats of combustion (multiplied by the molecular weight) and of the fact that resonance energies are obtained as small differences of two large figures. Fortunately, most of the thermochemical measurements on quinones and the respective hydroquinones were carried out by the same investigator, Valeur[5]; therefore, the conclusion may be justified that any consistent errors inherent in the methods and any correction factors, usually applied to values of heats of combustion of the French school of thermochemists, will be cancelled, since the difference of two energy terms is always taken. A different source of error stems from the estimation of the heats of sublimation, or rather the difference of the heats of sublimation of the quinone and hydroquinone, necessary for the computation of the difference in resonance energies. Coolidge and Coolidge[6] have measured the heats of sublimation of a number of quinones and hydroquinones, and their measurements show that in almost all cases the hydroquinone has the higher heat of sublimation, which is possibly a result of hydrogen bonding. The difference in the heats of sublimation is in the order of 8 kcal. per mole in favor of the hydroquinone, and this value is used in the present calculations whenever the experimental value was not known. Another set of data was obtained from the temperature coefficient of the potential as measured for many quinones by Conant and Fieser.[7] From the temperature coefficient these authors calculated the difference in total heat content (ΔH) of the reduction, and compared the values with the difference in heat content obtained from the thermochemical data of Valeur. Since the ΔH values represent the difference in heat of formation of the quinone and the hydroquinone, they are directly comparable with thermochemical data and can be used to evaluate the difference in empirical resonance energies of the two compounds. Thus in the case of benzoquinone the difference in resonance energies is 38.2 kcal. as calculated from heats of combustion[8] and the known heats of sublimation[6]; Conant and Fieser's value of 42.5 kcal. for the temperature coefficient leads to almost the same figure of 37.9 kcal. for the difference in resonance energies. In the latter case allowance has to be made not only for the heat of sublimation, but also for the heat of solution,[8] because the temperature coefficient is measured in solution. It is only in the case of benzoquinone that all necessary experimental data are known and that it is possible to compare the two methods.

The results of the calculations are summarized in Table I. The first column lists a number of quinones; column two contains the oxidation-reduction potentials as measured by Conant and Fieser at 25° in alcoholic solution. In column three are listed the differences in resonance energies of the hydroquinones and the quinones obtained from heats of combustion of Valeur, corrected by Swietoslawski,[9] or obtained from the temperature coefficients. Column four contains

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[3] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 2nd ed., 1944, p. 53.

[4] Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 75.

[5] Valeur, *Ann. chim. phys.*, [7] **21**, 470 (1900).

[6] Coolidge and Coolidge, This Journal, **49**, 100 (1927).

[7] Conant and Fieser, *ibid.*, **44**, 2480 (1922); **45**, 2194 (1923); **46**, 1858 (1924); Conant, *ibid.*, **49**, 293 (1927).

[8] Berner, *Z. physik. Chem.*, **117**, 83 (1925), quoted by Schreiner.

[9] Swietoslawski and Starczewska, *J. chim. phys.*, **22**, 399 (1925); Landolt–Börnstein, "Physik. Chem. Tabellen," Erster Ergänzungsband, 1927, p. 870.

the normal potential expressed as the free energy of reduction. If the small differences in the empirical resonance energies are sufficiently reliable to permit comparison, the anticipated relationship between the difference in resonance energies and the potential seems to exist; the potential gradually decreases as the energy difference becomes smaller. In other words, benzoquinone is a good oxidizing agent, *i. e.*, it is easily reduced, because of the large difference of 38 kcal. in the resonance energies of the quinone and the hydroquinone, whereas anthraquinone, which is almost as stable as anthrahydroquinone, does not have the tendency to pass over easily into its reduction product, because the gain in stabilizing resonance energy is much less.

TABLE I

I	II π_{25}, volt	III ΔRE, kcal.	IV ΔF, kcal.
Chlorobenzoquinone[a]	0.736	40	33.9
Benzoquinone	.711	38	32.7
Toluquinone	.656	35	30.2
p-Xyloquinone[a]	.597	34	27.5
p-Thymoquinone	.589	31	27.1
1,2-Naphthoquinone[a,b]	.579	31	26.7
Potassium-1,4-naphthoquinone-3-sulfonate[a,c]	.553	30	25.5
1,4-Naphthoquinone[b]	.493	27	22.7
2-Methyl-1,4-naphthoquinone[b]	.408[d]	21	18.8
Anthraquinone[e]	.155	8	7.1

[a] From the temperature coefficient; the difference in heat of solution was taken as 1 kcal. in favor of the quinone. [b] The heats of combustion of 1,4-naphthohydroquinone, 2-methyl-1,4-naphthoquinone and 2-methyl-1,4-naphthohydroquinone were determined by Dr. James L. Crenshaw and Miss Senta Amon in these laboratories using an oxygen bomb calorimeter. The following values for the heats of combustion were found: 1,4-naphthohydroquinone, 1137, 1144; 2-methyl-1,4-naphthoquinone, 1252, 1253; 2-methyl-1,4-naphthohydroquinone, 1292, 1302. The values used in the above calculations are: 1140, 1252 and 1297 kcal. [c] The potassium sulfonate group, for which the resonance energy cannot be calculated by the above methods, was neglected, since it was assumed that this group would contribute identical amounts to the resonance energies of both the quinone and hydroquinone. [d] Fieser and Fieser, THIS JOURNAL, 57, 491 (1935). The potential is determined in 70% alcoholic solution. [e] The value for the heat of combustion of anthrahydroquinone is not known; the above value was obtained by adding 14 kcal. as the contribution of two hydroxyl groups to 105 kcal., the value given by Pauling for the resonance energy of anthracene (ref. 3, p. 136). The value for anthraquinone is taken from Pauling and Sherman, *J. Chem. Physics*, 1, 615 (1933).

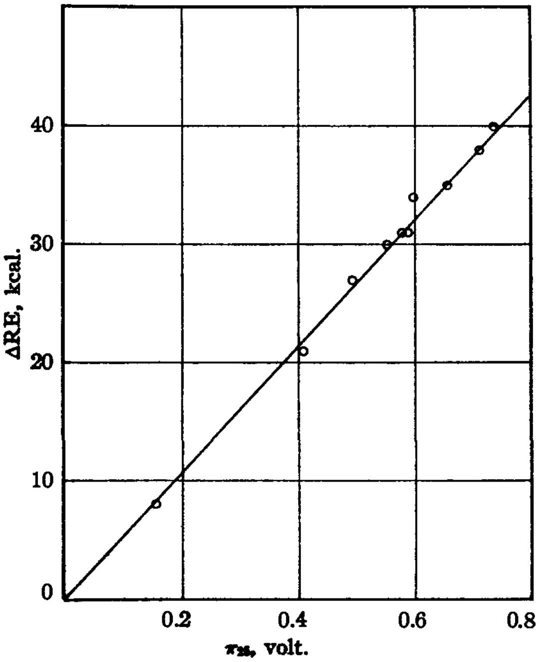

Fig. 1.

The graph (Fig. 1) shows the difference in resonance energies plotted against the oxidation–reduction potentials; a fairly straight line is obtained, as is the case in the calculations of Branch and Calvin. In view of the rather crude methods by which the differences in resonance energies were obtained, and the possible errors in the estimation of some of the values, a further interpretation of the data, or a more quantitative comparison, does not seem to be justified and is not attempted.

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Summary

The difference in empirical resonance energies of a number of quinones and the respective hydroquinones has been computed from known experimental data. A relationship exists between the difference in resonance energies of the quinones and the respective hydroquinones and the oxidation–reduction potential.

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